


FORM PTO-1390		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 3095-004
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/937850
INTERNATIONAL APPLICATION NO. PCT/IN00/00013	INTERNATIONAL FILING DATE 16 February 2000 (16.02.2000)	PRIORITY DATE CLAIMED 16 February 2000 (16.02.2000)	
TITLE OF INVENTION A MULTI STAGE SELECTIVE CATALYTIC CRACKING PROCESS AND A SYSTEM FOR PRODUCING HIGH YIELD OF MIDDLE DISTILLATE PRODUCTS FROM HEAVY HYDROCARBON FEEDSTOCKS			
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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) 6. <input type="checkbox"/> A English translation of the International Application into English (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154 371 (c)(2) 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendment has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A English translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A English translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 			
Items 11. to 20. below concern other document(s) or information included:			
<ol style="list-style-type: none"> 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input checked="" type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4) 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4) 20. <input type="checkbox"/> Other items or information. <ol style="list-style-type: none"> a. 			

met, a petition to revive (37 CFR 1.137(a) or (b))



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DOCKET No. 3095-004

09/937850 #5
Rec'd PCT/PTO 30 JUL 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Debasis BHATTACHARYYA, et al.

Serial No.: not yet assigned

Group Art Unit: not yet assigned

Filed: September 28, 2001

Examiner: not yet assigned

For: A MULTISTAGE SELECTIVE CATALYTIC CRACKING PROCESS AND A
SYSTEM FOR PRODUCING HIGH YIELD OF MIDDLE DISTILLATE PRODUCTS
FROM HEAVY HYDROCARBON FEEDSTOCKS

PRELIMINARY AMENDMENT

Honorable Assistant Commissioner
For Patents
Washington, D. C. 20231

Sir:

IN THE SPECIFICATION:

Kindly substitute the attached SUBSTITUTE SPECIFICATION for the specification as originally filed. No prohibited new matter has been introduced in this substitute specification. A copy of the original specification, interlineated with the changes introduced in the Substitute Specification is attached hereto as an appendix.

IN THE CLAIMS:

In advance of prosecution, kindly cancel all of the originally filed claims and substitute the following claims therefore:

21. (NEW) A multi stage selective catalytic cracking process, for producing high yield of middle distillate products having carbon atoms in the range of about C_8 to C_{24} from heavy hydrocarbon feed stocks in the absence of added hydrogen, said process comprising the steps of:

- i) contacting preheated feed stock with a mixed catalyst in a first riser reactor under catalytic cracking conditions including catalyst to oil ratio of about 2 to 8, WHSV of about $150-350 \text{ hr}^{-1}$, contact period of about 1 to 8 seconds and top temperature in the range of about 400°C to 500°C , to obtain first cracked hydrocarbon products;
- ii) separating the first cracked hydrocarbon products from the first riser reactor into a first fraction comprising hydrocarbons with boiling points less than or equal to about 370°C and a second fraction comprising hydrocarbons with boiling points greater than or equal to about 370°C , comprising unconverted hydrocarbons;
- iii) cracking the second fraction from the first riser reactor comprising hydrocarbons having boiling points greater than or equal to about 370°C , in the presence of regenerated catalyst, in a second riser reactor operating under catalytic cracking conditions including WHSV of about $75-275 \text{ hr}^{-1}$, catalyst to oil ratio of about 4-12 and riser top temperature of about $425 - 525^\circ\text{C}$ to obtain second cracked hydrocarbon products;
- iv) separating the catalytically cracked products from the second riser reactor alongwith the cracked products comprising hydrocarbons having boiling points less than or equal to about 370°C , from the first riser reactor to yield cracked products comprising dry gas, LPG, gasoline, middle distillates, heavy cycle oil and slurry oil;
- v) recycling substantially the entire heavy cycle oil comprising hydrocarbons having boiling points in the range of about 370°C to 450°C and at least part of the slurry

oil having boiling points greater than or equal to 450°C, into the second riser reactor at a vertically

displaced position lower than the position of introduction of the main feed, comprising bottom unconverted hydrocarbon fraction having boiling points greater than or equal to about 370°C, from the first riser reactor to obtain middle distillate products comprising hydrocarbons having carbon atoms in the range of C₈ - C₂₄ in a proportion of about 50 to 65 wt % of the feed stock,

22. (NEW) A process as claimed in claim 21 wherein, the feed stock is at least one petroleum based heavy feed stock selected from the group consisting of vacuum gas oil (VGO), visbreaker/cooker heavy gas oil, cooker fuel oil and hydrocracker bottom.

23. (NEW) A process as claimed in claim 21 wherein the feed stock is preheated to a temperature of about 150-350°C and then injected into a pneumatic flow riser type cracking reactor

24. (NEW) A process as claimed in claim 21 further comprising mixing spent catalyst is with the regenerated catalyst and charging the mixed catalyst, with a coke content of about 0.2 to 0.8 wt% of catalyst, to the bottom of the first riser at a temperature of about 450 - 575°C.

25. (NEW) A process as claimed in claim 21 wherein the cracked hydrocarbon vapor products from the first and second risers are separated from their respective spent catalysts under conditions sufficient to minimize over cracking of middle distillate range products into lighter hydrocarbons.

26. (NEW) A process as claimed in claim 21 wherein the spent catalysts from the first and second riser reactors are passed through respective dedicated catalyst strippers under conditions sufficient to render the catalysts substantially free from entrained hydrocarbons.

27. (NEW) A process as claimed in claim 21 wherein the regenerated catalyst with coke content of less than 0.4 wt% is obtained by burning coke off a portion of the spent catalyst from the first stripper, the spent catalyst from the second stripper or the common stripper in a turbulent or fast fluidized bed regenerator in the presence of air or oxygen containing gases at a temperature in the range of about 600°C to 750°C.

28. (NEW) A process as claimed in claim 21 wherein the catalyst is continuously circulated through standpipe and slide valves between the fluidized bed riser reactors, strippers and the common regenerator.

29. (NEW) A process as claimed in claim 21 wherein the catalytic cracking conditions in the first reactor, including feeding mixed regenerated catalyst, result in very high selectivity of middle distillate range products and conversion of hydrocarbon products of boiling point less than or equal to about 370°C at lower than about 50 wt% of the fresh feed.

30. (NEW) A process as claimed in claim 21 wherein the catalyst comprises a mixture of ReUSY zeolite based catalyst, having fresh surface area of 110-180 m²/gm., pore volume of 0.25-0.38 cc/gm and average particle size of 60-70 microns, with selective acidic bottom upgrading components in the range of about 0-10 wt%.

31. (NEW) A process as claimed in claim 21 wherein the unconverted heavy hydrocarbon fraction from the second riser that is recycled into the second riser comprises about 0-50 wt% of the main feed to the second riser.

32. (NEW) A process as claimed in claim 21 wherein the amount of steam used for feed dispersion and atomization, and catalyst lifting at the riser bottom in the first and the second riser reactors is about 1-20 wt% of the respective total hydrocarbon feed.

33. (NEW) A process as claimed in claim 21 wherein the spent catalyst resides in the stripper for a period of up to about 30 seconds.

34. (new) A process as claimed in claim 21 wherein the regenerated catalyst fed to the bottom of the second riser reactor has about 0.1-0.3 wt% coke, has a temperature of about 600-750°C and is lifted by catalytically inert gases.

35. (NEW) A process as claimed in claim 21 wherein the combined Total Cycle Oil (150-370°C) product, which is a mixture of heavy naphtha (150-216°C) and light cycle oil (216-370°C), has higher cetane number than that from distillate produced in an FCC unit operated in a conventional distillate mode and specific gravity, viscosity, pour point that are in the same range as that of distillate produced by a commercial FCC unit operating in a distillate mode.

36. (new) A process as claimed in claim 21 wherein changing the cut point of the TCO from the first riser to 120-370°C, processing 370°C+ part of the first riser product in the second riser, and changing the cut point of TCO from the second riser to 120-390°C, increases the yield of the overall combined TCO product by 8-10 wt%, and wherein the combined TCO product has substantially the same properties, but improved cetane number, as that of TCO obtained from a commercial FCC unit operating in a distillate mode.

37. (NEW) A process as claimed in claim 21 wherein the Total Cycle Oil comprises a mixture of heavy naphtha hydrocarbons having boiling points of about 150°C to 216°C and light cycle oil hydrocarbons having boiling points of about 216°C to 370°C.

38. (NEW) A fluidized bed catalytic cracking system, for the production of high yield of middle distillate products comprising hydrocarbons having carbon atoms in the range of C₈ to C₂₄ from heavy petroleum feeds, comprising:

- A. at least two riser reactors (1 and 2) means to introduce a fresh feed into the first riser reactor (1);
- B. means, at the end of the first riser reactor (1), to quickly separate the spent catalyst from hydrocarbon product vapors;
- C. means to steam strip said spent catalyst under conditions sufficient to remove entrained hydrocarbons;
- D. first conduit means (5), adapted to:

- feed a part of the said stripped catalyst into a regenerating apparatus (7), and feed another part of the stripped catalyst into a mixing vessel (10);
- E. second conduit means (19) adapted to feed mixed catalyst to a point proximate to the bottom of the first riser reactor (1)
- F. third conduit means (12) adapted to feed hydrocarbon product vapors separated from the catalyst evolved from said first riser reactor to a distillation column (13);
- G. means to separate first cracked hydrocarbon products into a first fraction comprising hydrocarbons having boiling points not greater than about 370°C and a second fraction comprising hydrocarbons with boiling points not less than about 370°C, including uncracked feed fractions;
- H. feed nozzle means (16) to feed said second fraction, comprising uncracked hydrocarbon products, into the bottom of said second riser reactor (2) at a point above the regenerated catalyst entry zone;
- I. means to feed regenerated catalyst from the regenerating apparatus (7) to the bottom of the second riser reactor (2) through a conduit (9);
- J. means to separate the hydrocarbon products of the second riser reactor (2) from the spent catalyst;
- K. means to separate the cracked products of the second riser reactor (2), along with the products of the first fraction of the first riser reactor (1) comprising hydrocarbons with boiling points not greater than about 370°C into fractions comprising dry gas, LPG, gasoline, heavy naphtha, light cycle oil, heavy cycle oil, and slurry oil; .
- L. means, including a separate feed nozzle (17) located at a point lower than the position of introduction of main feed, to recycle substantially all of the heavy cycle oil and at least part of the slurry oil, comprising hydrocarbons with boiling points of at least about 370°C, to said second riser reactor (2);
- M. means to pass the feed and cracked product vapors together with said catalyst, into the second riser;
- N. means to separate spent catalyst from product vapors of the second riser reactor (2) ;
- O. means to strip entrained hydrocarbons from spent catalyst;

- P. means to conduct stripped catalyst through a conduit (18) into the regenerating apparatus (7);
- Q. means to regenerate said stripped catalyst and to produce a hot regenerated catalyst;
- R. means to separate said hot regenerated catalyst into two parts, means to pass one part of said hot regenerated catalyst to the mixing vessel (10) through a conduit (8) and means to pass the other part of said hot regenerated catalyst directly to the bottom of the second riser reactor (2);
- S. means to pass the mixed catalyst from the mixing vessel (10) through a conduit (19) to the inlet of the first riser reactor (1);
- T. means to control:
the catalyst bed level in said stripping means,
the catalyst circulation rate from the common regenerator, and
the quantity of the spent and regenerated catalyst entering into the mixing vessel (10) using slide valves placed in said conduits; and
thereby producing a high yield of middle distillate products.

39. (NEW) A system as claimed in claim 38 wherein the separating device includes at least one cyclone separator.

40. (NEW) A system as claimed in claim 38 further comprising means to maintain the pressure in the first and second riser reactors in the range of about 1.0 to 4.0 kg/cm²(g).

41. (NEW) The process claimed in claim 21 further comprising

(vi) recycling the fraction of unconverted hydrocarbons with boiling points greater than or equal to 370°C, obtained in step (iv) in additional riser reactors by repeating steps (iii) to (iv) to obtain additional middle distillate products.

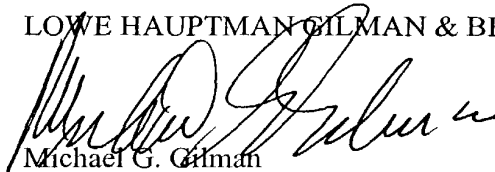
REMARKS

Favorable consideration of the patentability of the new claims of the above identified patent application is solicited. These new claims do not introduce any prohibited new matter.

It is believed that the fee being paid herewith is complete and sufficient to cover any matters for which a fee is due. However, should any additional fee be required, or should there have been an overpayment of the fee filed herewith, kindly debit or credit the underage or overage to the undersigned attorneys' deposit account 07-1337.

Respectfully submitted,

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September 28, 2001

APPENDIX

INTERLINEATED SUBSTITUTE SPECIFICATION

A MULTI STAGE SELECTIVE CATALYTIC CRACKING PROCESS AND A SYSTEM FOR PRODUCING HIGH YIELD OF MIDDLE DISTILLATE PRODUCTS FROM HEAVY HYDROCARBON FEEDSTOCKS

Field Of The Invention

This invention relates to a process and a system for the improved production of middle distillate products comprising hydrocarbons having carbon atoms in the range of C_8 to C_{24} in high yield, from heavier petroleum fractions through multistage catalytic cracking of varying severity levels with solid acidic catalyst without using external hydrogen.

Background Of The Invention

Conventionally, middle distillate range products, e.g. heavy naphtha, kerosene, jet fuel, diesel oil and light cycle oil (LCO), are produced in petroleum refineries by atmospheric/vacuum distillation of petroleum crude and also by the secondary processing of vacuum gas oil and residues or mixtures thereof. Most commonly practiced commercial secondary processes are Fluid Catalytic Cracking (FCC) and Hydrocracking. Hydrocracking employs porous acidic catalysts similar to those used in catalytic cracking but associated with hydrogenation components such as metals of Groups VI and VII of the Periodic Table to produce good quality of middle distillate products in the boiling range of C_8 - C_{24} hydrocarbons. An excess of hydrogen is supplied to the hydrocracking reactor under very high pressure (150-200 atm.) and at a relatively lower temperature (375-425°C) in fixed bed reactors with two phase flow. Due to severe hydrogenation, all hydrocarbon products from Hydrocracker are highly saturated with low sulfur and aromaticity. The yield of middle distillate hydrocarbons (126-391°C boiling range) in hydrocracking is typically very high, i.e. up to 65 - 80 wt% of feed.

FCC process, on the other hand, is employed for producing substantial quantities of high octane gasoline and LPG. In countries where demand for middle distillate product is higher,

heavy cracked naphtha (HCN: $C_8 - C_{12}$ hydrocarbons) and light cycle oil (LCO: $C_{13} - C_{24}$ hydrocarbons) production are maximized by manipulating operating variables so as to vary the reaction and regenerator severity levels. U.S. Patent Nos. 3,894,931 and 3,894,933 address such operations. Typically, diesel yield in FCC is maximized by maintaining a lower reaction and regeneration severity and recycling of unconverted residual products. Catalysts with lower zeolite/matrix ratio and MAT (Micro Activity Test) activity of about 60-70 is normally preferred. By proper selection of FCC variables and innovations involving catalyst type and recycle of [H]heavy [C]ycle [O]il and residual [S]lurry oil, distillate yield can be increased by considerable amount at the expense of Gasoline yield. As the FCC unit operation is shifted from gasoline mode to middle distillate maximization mode, the LCO cetane number increases and thus could be more useful for blending into the diesel pool.

However, while running at low severity operations[,] for maximizing diesel yield, the unconverted bottom yield also increases to a significant extent and sometimes may even exceed 20 wt% of fresh feed, as against 5-6 wt% for the usual gasoline mode operation. The other drawback of low severity operation is in the high amount of recycle oil being [used in the riser]fed to the bottom of the riser with fresh feed for further cracking. Firstly, this reduces the throughput of riser reactor and secondly, with a single riser and product fractionator, the recycle is nonselective. Consequently, [D]diesel yield from FCC with [the]a conventional cracking catalyst could be maximized up to 40-45 wt% in spite of running at low reaction severity (495°C riser temperature) and fairly high recycle ratio (30% of fresh feed).

Besides the operation of conventional FCC in middle distillate maximization mode, there are several other processes aiming for improvement in middle distillate yield. U.S. Pat. No. 5,098,554 discloses a process of fluid catalytic cracking with multiple feed injection points where fresh feed is charged to upper injection points and unconverted slurry oil is recycled to a location below the fresh feed nozzles. Essentially, the process conditions are similar to that of gasoline mode FCC operation (e.g., 527°C riser top temperature) which favors gasoline production. By adopting split feed injection, middle distillate yield is marginally increased at the expense of [G]gasoline yield.

U.S. Pat. No. 4,481,104 describes about an ultra-stable Y-zeolite, of high framework silica to alumina ratio having low acidity[,]and large pores, use of which in catalytic cracking of gas oil, enhances distillate yield. It may be noted that yield of 420 – 650°F fraction is maximize about 28 wt% of feed and, as 650°F- conversion increases beyond 67 wt%, the yield of 420– 650°F fraction reduces. Therefore, as discussed earlier, yield of the distillate is relatively [more] higher only at the higher yield of unconverted fraction.

Yet another process, reported in U.S. Pat. No. 4,606,810, discloses a scheme of two riser cracking for improving total gasoline plus distillate yield. Here, the feed is first cracked in the first riser with spent catalyst from the second riser and the unconverted part is further cracked in a second riser in presence of regenerated catalyst. The basic operation is of high severity producing maximum amount of [G]gasoline and the yield of LFO is around 15 – 20 wt% of feed. It may also be noted that while increase in [G]gasoline yield is in the range of 7.5 – 8.0 wt%, increase in LFO yield is merely in the range of 1.5 – 3.0 wt% on fresh feed basis.

Two stage processing of hydrocarbon feedstock has been employed by different researchers in the field of catalytic cracking. Several processes have been developed in which first stage processing removes metals and Conradson Carbon Residue (CCR) impurities from feed using a low activity cheap contact material with abundant surface area. The demetallized feed is then processed in a more conventional second stage reactor under high severity conditions to maximize the conversion and gasoline production. U.S. Pat. No. 4,436,613 describes such a process of two stage catalytic cracking using two different types of catalyst. In the first stage, the CCR materials and metals are separated from the rest of the feedstock along with mild cracking over a relatively lower activ[e]ity catalyst. The residual un-cracked product of the first stage is then contacted with a high activ[e]ity catalyst under higher reaction severity for gasoline maximization. It may be noted that in this process, two dedicated strippers and regenerators are used to avoid the mixing of two different types of catalysts.

Dual riser high severity catalytic cracking process described in U.S. Pat. No. 3,928,172 utilizes a mixture of large pore REY zeolite catalyst and a shape selective zeolite catalyst where

gas oil is cracked in the first riser in the presence of the aforesaid catalyst mixture. The [H]heavy [N]naphtha product from the first riser and/or virgin straight run [N]naphtha are cracked in the second riser in the presence of catalyst mixture to produce high octane [G]gasoline together with C₃ and C₄ olefins. U.S. Pat. No. 4,830,728 discloses a process for upgrading straight run [N]naphtha, catalytically cracked [N]naphtha and mixtures thereof in a multiple fluid catalytic cracking operation utilizing mixture of amorphous cracking catalyst and/or large pore Y-zeolite based catalyst and shape selective ZSM-5 zeolite catalyst to produce high octane gasoline.

U.S. Pat. No. 5,401,387 describes a process of multistage catalytic cracking where the first stage cracks a first feed over a shape selective zeolite to produce lighter products rich in iso-compounds which may be used for making ethers. A second feed, which may include 700°F+ liquid from first stage, is cracked in the second stage. Another process, as described in U.S. Pat. No. 5,824,208, discloses a scheme in which hydrocarbon is initially contacted with cracking catalyst forming a first cracked product which, after recovering of the product fraction having boiling point of more than 430°F, is subjected to cracking in a second riser. The basic objective of this invention is to maximize the yield of light olefins and minimize the formation of aromatic compounds by avoiding undesirable hydrogen transfer reactions.

So far, most of the prior art methods have concentrated on multiple riser catalytic cracking for maximization of gasoline yield and its octane numbers, increased yield of iso-olefin for production of ethers, increased yield of light olefins, etc. From the prior art information and also from our experience of operating low severity FCC units, it is quite clear that maximizing middle distillate yield in FCC (without using external hydrogen) is not achieved beyond a level of 40-45 wt% of fresh feed. Further, persons involved in fluid catalytic cracking would be aware that middle distillate, being an intermediate product in the complex catalytic cracking reactions, [its maximization] is very difficult to maximize because, when the severity is increased, it is over cracked to lighter hydrocarbons.

Objects

Accordingly, one object of the present invention aims to propose a novel catalytic cracking process for producing middle distillate products in very high yield (about 50–65 wt%).

Another object is to provide a multiple riser system that enables the production of middle distillate products, including heavy naphtha and light cycle oil in high yield.

Yet another object of the invention is to provide a multiple riser system to produce higher yield of [H]heavy [N]naphtha and [L]light [C]cycle [O]oil as compared to the prior art processes employing catalytic cracking of petroleum feedstock without any use of external supply of hydrogen.

A further objective of the process is to minimize the yield of unwanted dry gas and coke and also the yield of unconverted bottom products, at the same time, improving the cetane quality of the middle distillate product.

Brief Summary Of The Invention

According to the present invention, there is provided a novel process for catalytic cracking of various petroleum based heavy feed stocks in the presence of a solid zeolite catalyst and [high]large pore size acidic components for selective bottom cracking and mixtures thereof, in a multiple riser type system wherein continuously circulating fluidized bed riser reactors are operated at different severities to produce middle distillate products in high yield, that is in the range of about 50-65 wt% of fresh feed.

The invention also provides an improved system for catalytic cracking of heavy feed stock to obtain middle distillate products in high yield, employing the process herein described.

Detailed Description Of The Invention

The invention relates to a multi stage selective catalytic cracking process for producing high yield of middle distillate products having an average number of carbon atoms in the range of about C₈ to C₂₄, from heavy hydrocarbon feedstock, in the absence of added hydrogen, said process comprising the steps of:

- i) contacting preheated feed with a mixed catalyst in a first riser reactor, under catalytic cracking conditions including catalyst to oil ratio of about 2 to 8, WHSV of about 150-350 hr⁻¹, contact period of about 1 to 8 seconds and temperature in the range of about 400°C to 500°C, to obtain first cracked hydrocarbon products;
- ii) separating the first cracked hydrocarbon products from the first riser reactor into a first fraction comprising hydrocarbons with boiling points less than or equal to about 370°C and a second fraction comprising [unconverted]hydrocarbons with boiling points greater than or equal to 370°C that comprise unconverted feed material;
- iii) cracking the [unconverted]second fraction from the first riser reactor, comprising hydrocarbons having boiling points greater than or equal to 370°C, in the presence of regenerated catalyst, in a second riser reactor operating under catalytic cracking conditions, including WHSV of about 75-275 hr⁻¹, catalyst to oil ratio of about 4-12 and riser top temperature of about 425 - 525°C to obtain second cracked hydrocarbon products;
- iv) separating the catalytically cracked products from the second riser reactor, along with cracked products comprising hydrocarbons having boiling points less than equal to 370°C, from the first riser reactor, in a main fractionating column to yield cracked products comprising dry gas, LPG, gasoline, middle distillates, heavy cycle oil and slurry oil;
- v) recycling the entire heavy cycle oil, comprising hydrocarbons having boiling points in the range of about 370°C to 450°C, and full or part of the slurry oil, having boiling points greater than or equal to about 450°C, into the second riser

reactor at a vertically displaced position lower than the position of introduction of the main feed, comprising a bottom fraction comprising an unconverted hydrocarbon fraction, having boiling points greater than or equal to about 370°C, from the first riser reactor to obtain middle distillate products comprising hydrocarbons having carbon atoms in the range of about C₈ - C₂₄ ranging from about 50 to 65 wt % of the fresh feed [rate] into the first riser.

- iv) Optionally, recycling the fraction of unconverted hydrocarbons with boiling points greater than or equal to about 370°C, obtained in step (v), in riser reactor(s) by repeating steps (iii) to (iv), to obtain substantially pure middle distillate products.

In an embodiment, the feed stock is selected from petroleum based heavy feed stock, such as vacuum gas oil (VGO), visbreaker/cooker heavy gas oil, cooker fuel oil, hydrocracker bottoms, etc.

In another embodiment, mixed catalyst is obtained from an intermediate vessel used for mixing the spent catalyst from the common stripper, or preferably from a first stripper, with the regenerated catalyst from the common regenerator and charging the mixed catalyst, with coke content in the range of about 0.2 to 0.8 wt% to the bottom of the first riser at a temperature of 450 - 575°C.

In another embodiment, the exit hydrocarbon vapors from the first and second risers are quickly separated from respective spent catalysts using respective cyclones and/or other conventional separating devices to minimize the overcracking of middle distillate range products into less [un]desirable lighter hydrocarbons.

In yet another embodiment, the spent catalysts from the first and second riser reactors are passed through respective dedicated catalyst strippers or a common stripper to render the catalysts substantially free of entrained hydrocarbons.

In a further embodiment, the regenerated catalyst with coke content of less than 0.4 wt% is obtained by burning a portion of the spent catalyst from the first stripper, the spent catalyst from the second stripper or the common stripper in a turbulent or fast fluidized bed regenerator in the presence of air or oxygen containing gases at a temperature ranging from about 600°C to 750°C.

In another embodiment, the catalyst circulation between the fluidized bed riser reactors, strippers and the common regenerator is continuously [circulated] through standpipe and slide valves.

In yet another embodiment, the critical catalytic cracking conditions in the first reactor, including mixed regenerated catalyst, result in very high selectivity of middle distillate range products and conversion of hydrocarbon products of boiling point less than or equal to 370°C at lower than 50 wt% of the fresh feed.

In another embodiment, the zeolite cracking catalyst comprises commercial ReUSY zeolite based catalyst, having a fresh surface area of about 110-180 m²/gm., a pore volume of about 0.25-0.38 cc/gm and an average particle size of about 60-70 microns, along with selective acidic bottom upgrading components in the range of 0-10 wt%.

In still another embodiment, the unconverted heavy hydrocarbon fraction from the second riser, that is being recycled into the second riser, ranges from about 0-50 wt% of the main feed rate (i.e. 370°C+ fraction) from the first riser to the second riser, depending on the nature of the feedstock and operating conditions kept in the risers.

In yet another embodiment, the amount of steam used for feed dispersion and atomization in the first and the second riser reactors is in the range of about 1-20 wt% of the respective total hydrocarbon feed depending on the quality of the feedstock.

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In still another embodiment, by changing the cut point of the TCO from the first riser to 120-370°C, processing 370°C+ part of the first riser product in the second riser, and changing the cut point of TCO from second riser to 120-390°C, the yield of overall combined TCO product increases by 8-10 wt% and the combined TCO product has substantially the same properties, but improved cetane number, as that of TCO from commercial distillate mode FCC unit.

The invention is illustrated hereinbelow with reference to the following accompanying drawings, wherein:

Fig.2 shows a fluidized catalytic cracking two riser system of the present invention.

Fig.3 is a graph showing the ratio of TCO Yield/Yields of $([D]drygas+LPG+[G]gasoline+[C]coke)$ Vs. $-370^{\circ}C$ conversion with first riser feed at two different temperatures ($425^{\circ}C$ & $490^{\circ}C$).

Fig.4 is a graph showing the ratio of TCO Yield/Yields of $([D]drygas+LPG+[G]gasoline+[C]coke)$ Vs. $-370^{\circ}C$ conversion with second riser feed at two different temperatures ($490^{\circ}C$ & $510^{\circ}C$).

The reference numbers of the several figures of the drawing are unique to each figure.

Description of Fig.1 :

In the conventional Fluid Catalytic Cracking (FCC) unit, fresh feed (1) is injected at the bottom of the riser (2) whereupon it comes into contact with hot regenerated catalyst from the regenerator (3). The catalyst along with hydrocarbon feed and product vapors ascends the riser and at the end of the riser spent catalyst is separated from the hydrocarbon vapor and subjected to steam stripping. The hydrocarbon vapors from the riser reactor are sent to a main fractionator column (4) for separating into the desired products. The stripped catalyst is passed to a regenerator (3) where the coke deposited on the catalyst is burnt off and the clean hot catalyst is circulated back to the bottom of the riser.

The fluidized catalytic cracking two riser system of the invention is schematically shown in Fig. 2, and described in detail hereinbelow.

The fluidized bed (sometimes referred to as a transport bed) catalytic cracking system for the production of high yield of middle distillate products, comprising hydrocarbons having numbers of carbon atoms in the range of about C_8 to C_{24} , from heavy petroleum feeds, [by a process as defined in claim 1, said system comprising]comprises at least two riser reactors (1 and 2).[wherein a] A fresh feed is introduced into the first riser reactor (1), typically at the bottom section but above the regenerated catalyst entry zone through a feed nozzle (3).[and at] At the end of the first riser reactor (1), the spent catalyst is quickly separated from hydrocarbon product vapors using separating devices (4), and the separated catalyst is subjected to multistage steam stripping to remove any entrained hydrocarbons.[and a] A conduit (5) feeds a part of the said

stripped catalyst into a regenerating apparatus (7) and [the]another part of the stripped catalyst from the conduit (5) travels through another conduit (6) into a mixing vessel (10).[and thereafter] Thereafter, the mixed catalyst from the mixing vessel (10) travels through a conduit (19) and is fed to the bottom of the first riser reactor (1). [t]The hydrocarbon product vapors from the first riser reactor (1), which are separated from the catalyst in the separating devices (4), are fed to a vacuum or atmospheric distillation column (13) through conduit (12) whereby the first cracked hydrocarbon products are separated into a first fraction, comprising hydrocarbons having boiling points less than or equal to 370°C, and a second fraction, comprising uncracked hydrocarbons with boiling points greater than or equal to 370°C which includes uncracked hydrocarbons. [t]The said second fraction, comprising uncracked hydrocarbon products, is fed through feed nozzle (16) into the bottom of a second riser reactor (2) above the regenerated catalyst entry zone, and the regenerated catalyst from the regenerating apparatus (7) is fed to the bottom of the second riser reactor (2) through a conduit (9). [and subsequently] Subsequently, the hydrocarbon products of the second riser reactor (2) are separated from the catalyst, in separating devices (11), and the cracked products of the second riser reactor (2), along with the products of the first fraction of the first riser reactor (1) comprising hydrocarbons with boiling points less than or equal to 370°C, are fed to a main fractionator column (15) [which]that conventionally separates the said products into dry gas, LPG, gasoline, heavy naphtha, light cycle oil, heavy cycle oil, and slurry oil. The[and the]entire heavy cycle oil and [full]all or part of the slurry oil, consisting mainly of hydrocarbons with boiling points greater than or equal to 370°C, are recycled back to the second riser reactor (2) through a separate feed nozzle (17) located at a point lower than the position of introduction of main feed. The[,and the] feed and cracked product vapors travel along with the catalyst, [into]through the riser reactor [wherein]whereupon the spent catalyst is separated from product vapors of the second riser reactor (2) in separating devices (11), and the spent catalyst is subjected to multistage steam stripping for removal of entrained hydrocarbons. The [and the] stripped catalyst travels through a conduit (18) into the regenerating apparatus (7), wherein the coke on catalyst is burnt in the presence of air and/or oxygen containing gases at high temperature, and the flue gas from regeneration is separated from the entrained catalyst fines in separating devices (20) and the flue gas leaves from top of the regenerating apparatus (7) through a conduit (21) for heat recovery and venting through stack. The[;the] hot regenerated

catalyst is withdrawn from the regenerating apparatus (7) and divided into two parts, one going to the mixing vessel (10) through the conduit (8) and the other directly to the bottom of the second riser reactor (2).[,and the] The mixed catalyst from the mixing vessel (10) is fed through the conduit (19) to the inlet of the first riser reactor (1). The level of the catalyst bed is controlled [controlling the catalyst bed level] in the individual or common stripper. The[,the] catalyst circulation rate from the common regenerator and the quantity of the spent and regenerated catalyst entering into the mixing vessel (10) is controlled using slide valves placed [on]in the conduits and thereby producing high yield of middle distillate products.

At the bottom 'Y' section of both the risers (1 & 2), steam is used to lift the catalyst in upward direction up to the feed entry zone. Also steam is used in the feed nozzles (3, 16 & 17) for atomization and dispersion of the feed. The quantity of the steam flow into the respective risers (1&2) is varied depending on the feedstock quality and the desired velocity in the risers.

As an example, a system designed to practice the process of the invention has been described employing only two riser reactors. It is pertinent to note that in practice, riser reactors of any desired number may be functionally attached downstream of the second riser reactor so that the unconverted hydrocarbons obtained from the second riser may be further treated in accordance with the process described hereinabove and eventually, substantially pure middle distillate products may be obtained in high yield from the original feed.

In catalytic cracking processes using zeolite based catalyst, the reactions proceed sequentially. Middle distillate yield can be increased, if [it's]cracking thereof to lighter products is restricted. Any attempt in this regard is likely to reduce the conversion, resulting in higher yield of unconverted products. Conventionally, recycling of unconverted fraction has been practiced to improve the overall conversion. The severity required for cracking of the unconverted recycled fraction is adequate to produce significant quantity of gasoline and LPG by over-cracking of middle distillate range product. It also promotes hydrogen transfer reactions producing aromatics in middle distillate range products and therefore, deteriorates the cetane

quality. To summarize, it may be noted that maximization of intermediate product middle distillate by a cracking reaction is more challenging as compared to maximization of gasoline.

In distinction to other prior art processes, the present invention provides a process for producing maximized quantity middle distillate through catalytic cracking of heavy hydrocarbon fractions employing multiple risers. The applicants realized that the middle distillate selectivity is higher only at lower conversion. In fact, the ratio of yield of [T]_{total} [C]_{cycle} [O]_{oil} (TCO:150-370°C) to the sum of other products, (such as, dry gas, LPG, gasoline and coke) increases as the conversion reduces. Moreover, riser temperature has dramatic impact on the selectivity. At same conversion, the applicants have found that middle distillate selectivity improves significantly as riser temperature is reduced. The applicants have also investigated the role of coke on regenerated catalyst (CRC) and discovered that there is an optimum CRC for maximum yield of TCO (Ref.: Ind. Chem. Res., 32, 1081, 1993). Finally, the applicants have arrived at some specific conditions (comprising lower riser temperature, low contact time, low catalyst oil ratio, higher CRC, etc.) and type of the catalyst with which yield of TCO is maximized.

According to the present invention, petroleum feed stocks, such as [V]_{vacuum} [G]_{gas} [O]_{oil} (VGO), [C]_{coker} fuel oil, [C]_{coker}/[V]_{visbreaker} heavy gas oil, [H]_{hydrocracker} bottom, etc., are [is] catalytically cracked in presence of solid zeolite catalyst with or without selective acidic bottom cracking components in multiple riser-reactors. The feed is first preheated [at]_{to} a temperature in the range of about 150-350°C and then injected into a pneumatic flow, riser type cracking reactor with a residence time of about 1-8 seconds, and preferably of about 2-5 seconds. At the exit of the riser, hydrocarbon vapors are quickly separated from catalyst for minimizing the over cracking of middle distillate to lighter products.

The product from the first riser is separated in a fractionator into at least two streams, one comprising hydrocarbons having boiling points below about 370°C and the other comprising hydrocarbons having boiling points greater than about 370°C. The removal of hydrocarbon products having boiling points less than or equal to about 370°C [products] reduces the chance of

over-cracking of middle distillate range molecules to lighter products. The [unconverted]fraction, comprising hydrocarbons, including unconverted hydrocarbons, having boiling points greater than or equal to about 370°C, [fraction]from the first riser is pre-heated and then injected to the second riser reactor with residence time of about 1-12 seconds, and preferably in the range of about 4-10 seconds, through the feed nozzles located at a higher elevation. In the second riser, the regenerated catalyst is contacted with the recycle stream of unconverted heavy hydrocarbons from the second riser at a relatively lower elevation of the riser. This allows preferential cracking of the recycle components under high severity conditions (e.g., higher temperature, higher dynamic activity of the catalyst owing to low coke on regenerated catalysts) at the bottom of second riser. Typically, recycle ratio is maintained in the range of about 0-50% of the feed throughput in the second riser.

Steam and/or water, in the range of 1-20 wt% of feed, is added for dispersion and atomization in both the risers depending on type of feedstock. The desired velocity in the risers, especially in the first riser, is adjusted by the addition of steam.

The hydrocarbon product vapor from the second riser is quickly quenched with water/another, cooler hydrocarbon fraction and separated for minimizing the post riser non-selective cracking. The product from the second riser and the product boiling below about 370°C from the first riser are separated in a common fractionator into several products, such as [D]dry gas, LPG, [G]gasoline, [H]heavy naphtha, [L]light [C]cycle [O]oil and cracked bottoms. Part of the [unconverted]bottom product, including unconverted hydrocarbon feed, (the 370°C+ fraction) from the second fractionator is recycled to the second riser and a remaining part is sent to rundown after removal of catalyst fines.

The spent catalyst, with entrained hydrocarbons from the riser exit, is then passed through a common or separate stripping section where counter current steam stripping of the catalyst is carried out to remove the hydrocarbon vapors from the spent catalyst. The catalyst residence time in the strippers is required to be kept in the lower side of preferably less than about 30 seconds. This helps to minimize undue thermal cracking reactions and also reduces the

possibility of over-cracking of middle distillate range products. Stripped catalyst is then passed to a common dense or turbulent fluidized bed regenerator where the coke on catalyst is burnt in presence of air and/or oxygen containing gases to achieve coke on regenerated catalyst (CRC) of lower than about 0.4 wt% and preferably in the range of about 0.1 - 0.3 wt%. A part of the regenerated catalyst is directly circulated to the second riser reactor via standpipe/slide valve at a temperature of 600 - 750°C.

As mentioned earlier, there is an optimum CRC at which maximum TCO yield is obtained. In order to extract maximum TCO from the first riser, CRC is required to be maintained at relatively higher level, for example in the range of 0.2– 0.8 wt% depending on catalyst and operating conditions. In the second riser, the desirable CRC is relatively lower (for example in the range of 0.1 – 0.3 wt%) in order to utilize the full activity potential of the catalyst. Also, the temperatures of the regenerated catalyst entering into the two risers are different. The lower temperature and higher CRC of the catalyst entering to the first riser is achieved by mixing a part of the stripped catalyst from the first riser/common stripper with regenerated catalyst in a separate vessel equipped with fluidization steam, and circulating the mixed catalyst to the bottom of the first riser via a stand pipe/slide valve. The mixed catalyst enters at the bottom of the first riser with a temperature in the range of about 450 - 575°C (preferably in the range 475 - 550°C) and CRC of lower than about 0.8 wt% (preferably in the range of 0.25 – 0.5 wt% depending on type of catalyst). Another option [of]for controlling the catalyst return temperature in the first riser is to employ a catalyst cooler so that catalyst/oil ratio [could]can be controlled [almost]substantially independently. However, the instant mixing vessel is preferred since it acts as second stage stripper and helps to adjust the coke level on the catalyst.

Prior to the injection of the 370°C+ fraction of the first riser product, the fresh regenerated catalyst is contacted with [the]a recycle stream [of]comprising unconverted hydrocarbons from the second riser at a relatively lower elevation of the riser. The recycle components are preferentially cracked at the high severity conditions prevailing in the second riser bottom before the injection of 370°C+ fraction of first riser product. Typically recycle ratio is maintained in the range of about 0 – 50% of the second reactor feed throughput depending on

the type of the feed to be processed and the conversion level in both the reactors. If the recycle [quantity]rate is less, it may be injected along with the main feed i.e., 370°C+ fraction of first riser product.

In the present invention, the first riser operates in the range of about 150 - 350 hr⁻¹ weight hourly space velocity (WHSV), about 2 - 8 catalyst to oil ratio, and about 400 - 500°C riser top temperature to convert the feedstock to selectively cracked product including 35 – 45 wt% min. TCO yield and 40 - 60 wt% 370°C+ (bottom) yield. The second riser operates in the range of about 75 - 275 hr⁻¹ WHSV, about 4 -12 catalyst to oil ratio and about 425 -525°C riser top temperature. The absolute pressures in both reactors are about 1 - 4 kg/cm² (g). Steam and/or water, in the range of about 1 - 20 wt% of feed, is added not only for dispersion and atomization of feed but also to attain the desired fluidization velocity in the risers, especially in the first riser bottom. It also helps in avoiding the coke formation or catalyst agglomeration.

Comparison of major process conditions of the process of the present invention with conventional FCC & multi stage process is shown below :

Table – 1

	Multistage process of the present invention				FCC Process
	first reactor		second reactor		
	Range	Preferred Range	Range	Preferred Range	Range
WHSV, hr ⁻¹	150 – 350	200– 300	75 – 275	120 – 220	125 -200
Catatyst/Oil ratio (w/w)	2 – 8	3 – 5	4 –12	5 – 8	4 - 8
Riser temp., °C	400 – 500	425 - 475	425 – 525	460 – 510	490- 540
Steam injection, wt% of feed	1 - 20	8 - 12	1 – 20	4 – 8	0 - 10

Use of multiple riser concepts is not new, as each researcher has employed it for different purposes. The present invention utilizes dual or multiple riser systems for the exclusive purpose of maximization of middle distillate products. Being an intermediate product, middle distillate range molecules have a tendency to undergo further cracking. There is always a trade off between maximization of an intermediate range product and minimization of bottom unconverted part. This invention includes the sequence of operation and operating conditions for control of over-cracking of middle distillate in the first riser and upgradation of heavier molecules to middle distillate in the second riser. This invention provides a novel scheme for operation of two or multiple risers at entirely different operating conditions with a common regenerator. Use of so much lower temperature cracking is unusual so far. However, the applicants have found that reaction temperature has a predominant effect on the over cracking of middle distillate range products. For example, at 40 wt% [of] 370°C- conversion, the wt% yield ratios of TCO and all other products, (i.e., [D]dry [G]gas, LPG, [G]gasoline & [C]coke) except TCO and bottom (subsequently referred as TCO/Rest ratio) are in the range of about 3.0 – 3.5 and about 1.5 – 1.8 at reaction temperatures of 425°C and 490°C respectively. The difference in the above ratio is narrowed down as the conversion increases (Figure-3).

Therefore, for maximizing TCO, low reaction temperature, low [and] catalyst to oil ratio, as well as low catalyst activity is desirable. The applicants identified that lower catalyst/oil ratio (2 - 8) and higher WHSV of (150 - 350 hr⁻¹) along with lower riser temperature in the first riser of the process of the present invention are very important to achieve a very low degree of over cracking for producing maximum middle distillate range components. The applicants also observed that the TCO/Rest ratio is significantly affected by the 370°C- conversion level. For example, for a given catalyst and reaction temperature, if 370°C- conversion is 40%, the TCO/Rest ratio is as high as 3.2 which comes down to about 1.3 when 370°C - conversion is increased to 70%. This shows that restricting the conversion in the first stage riser up to about 40 – 45% is very important to maximize the yield of middle distillate.

In the second riser, the operating conditions need to be different for upgradation of heavy material to lighter products. However, undue increase in severity parameters will lead to

conversion of the desired middle distillate to LPG and [G]gasoline. The applicants have discovered that operation at an intermediate severity as compared to gasoline maximization mode FCC operation is absolutely necessary. The applicants have also found that in order to reduce the yield of unconverted bottoms and improve the middle distillate selectivity, recycle to a lower elevated entry point at the bottom of the second riser is very much effective. This allows the cracking of the recycled heaviest fraction in [presence] effective contact with [of] regenerated catalyst at relatively higher temperature and lower CRC that improves the dynamic activity of the catalyst and offers maximum cracking of the recycled feed. After cracking of the recycled part, the catalyst temperature comes down due to utilization of part of the heat for vaporization and endothermic cracking reactions of the recycled feed. Also, the coke on catalyst increases which essentially blocks some of the active sites and thereby reduces the dynamic activity of the catalyst. The contacting of catalyst having relatively lower temperature and higher coke on catalyst with the main feed, comprising the hydrocarbon fraction from the first riser having boiling points greater than or equal to about 370°C, assists to improve the selectivity of middle distillate range products out of the second riser. This contacting pattern is highly effective in increasing the overall yield of the middle distillate and reducing yield of the unwanted slurry oil.

In the present invention, the delta coke (defined as the difference in coke content of spent and regenerated catalyst) is low due to lower coke make in the extremely low severity cracking in the first riser which is expected to keep the regenerator temperature at a relatively lower level as compared to the conventional FCC operation using similar type of feedstocks. However, overall lower catalyst to oil ratio is likely to compensate for this effect and thereby maintain the regenerator temperature at least [to]at the same level as that of conventional FCC as required for burning of coke [on]off the catalyst.

Further details of feedstock, catalyst, products and operating conditions of the process of the present invention are described below:

Feed Stock:

Feed stock for the present invention includes hydrocarbon fractions starting from carbon no. 20 to carbon no. 80. The fraction could be straight run light and heavy [V]vacuum [G]gas [O]oil, [H]hydrocracker bottom, [H]heavy [G]gas [O]oil fractions from [H]hydrocracking, FCC, [V]visbreaking or [D]delayed [C]coking. The conditions in the process of the present invention are adjusted depending on the type of the feedstock so as to maximize the yield of middle distillate. Details of the feedstock properties are outlined in the examples given hereinbelow. The above feed stock types are for illustration only and the invention is not limited in any manner to only these feed stocks.

Catalyst:

The [C]catalyst employed in the process of the present invention predominantly [consists of] comprises Y-zeolite in rare earth ultra-stabilized form. Bottom cracking components consisting of peptized alumina, acidic silica alumina or Y- alumina or a mixture thereof are also added to the catalyst formulation to produce synergistic effect towards maximum middle distillate production under the operating conditions as outlined above. It may be noted that both the first and second stage risers are charged with the same catalyst. The pore size range of the active components namely, Re-USY zeolite and bottom selective active materials are in the range of about 8 – 11 and 50 – 1000 angstroms respectively. The typical properties of the Y-zeolite based catalyst are given in Table-2.

Table – 2

Surface Area, m ² /g,	Fresh	110 – 180
	Steamed	100 – 140
% Crystallinity	Fresh	10 – 15
	Steamed	8 – 12
Unit Cell Size, °A	Fresh	24.35 – 24.75
	Steamed	24.2 – 24.6
Micro-pore area, m ² /g,	Fresh	65 – 100
	Steamed	60 – 90
Meso-pore area, m ² /g,	Fresh	45 - 80
	Steamed	40 - 50
Pore volume, cc/gm		0.25 – 0.38

In the process of the present invention, the active catalyst components are supported on relatively inactive materials [of] such as silica/alumina or silica-alumina compounds, including kaolinites. The active components could be mixed together before spray drying or separately binded, supported and spray-dried using conventional spray drying technique. The spray-dried micro-spheres are washed, rare earth exchanged and flash dried to produce finished catalyst particles. The finished micro-spheres containing active materials in separate particles are physically blended in the desired composition. The preferred range of physical properties of the finished fresh catalyst as required for the process of the present invention:

Particle size range, micron	:	20-120
Particle below 40 microns, wt%	:	< 20
Average particle size, micron	:	50-80
Average bulk density, micron	:	0.6 – 1.0

Typically, the above properties and other related physical properties, e.g., attrition resistance, fluidizability etc. are in the same range as used in the conventional FCC process.

Products:

The main products in the process of the present invention is the middle distillate components namely, [H]heavy [C]racked [N]naphtha (HCN : 150 – 216°C) and [L]light [C]ycle oil (LCO : 216 – 370°C). The sum total of these two fractions, which is [called]referred to as [T]total [C]ycle [O]il (TCO : 150 – 370°C) is obtained with a yield up to about 50 - 65 wt% of the feed. The other useful products of the process of this invention are LPG (5 - 12%) and [G]gasoline (15 - 25 wt%). A range of other product yields from first and second stage risers are summarized in the following Table - 3:

Table – 3

	Yield, wt% of feed		
	From first reactor	From second reactor	Combined yield from both first & second
Dry Gas (C ₁ + C ₂)	0.1 – 0.35	1-1.5	0.5 – 1.5
LPG (C ₃ + C ₄)	3 – 4	8 – 12	5 – 12
Gasoline (C ₅ – 150°C)	10 – 15	25 – 30	15 – 30
Heavy Naphtha, (150–216°C)	8 – 10	10 – 13	10 – 15
Light Cycle Oil, (216–370°C)	35 – 45	25 – 35	40 – 50
Total Cycle Oil (150–370°C)	45 – 50	30 – 40	50 – 65
Bottom (370°C+)	40 – 60	10 – 20	5 – 15
Coke	1 – 3	2 – 5	2 – 4

The invention and its embodiments are described in further detail hereunder, with reference to the following examples, which should not be construed to limit the scope of the invention in any manner. Various modifications of the invention that may be apparent to those skilled in the art are deemed to be included within the scope of the present invention.

Example-1 (PRIOR ART)**Yield of middle distillate at different conversions in conventional FCC operation**

This example illustrates the change in yield of the middle distillate product (TCO) at different conversion levels under conventional FCC conditions. -216°C conversion is defined as the total quantity of products boiling below 216°C including Coke. Similarly -370°C conversion is defined as the total quantity of products boiling below 370°C including Coke. The experiments were conducted in standard fixed bed Micro Activity Test (MAT) reactor described as per ASTM D-3907 with minor modifications indicated subsequently as modified MAT. The catalyst to be used is first steamed at 788°C for 3 hours in presence of 100% steam. The physico-chemical properties of the feed used in the modified MAT reactor are given in the following Table – 4 & 5.

Table – 4

Density @ 15°C, gm/cc	0.8953
CCR, wt%	0.32
Sulfur, wt%	1.12
Basic Nitrogen, PPM	366
Paraffins, wt%	44.4
Naphthenes, wt%	18.1
Aromatics, wt%	37.6
Nickel, PPM	< 1
Vanadium, PPM	< 1

The runs were taken at a reaction temperature of 495°C, feed injection time of 30 seconds with WHSV in the range of 40 – 120 hr⁻¹. Catalysts used in this example are catalyst A & B which are commercially available FCC catalyst samples having properties as shown in the Table-6.

Table – 7

Product Yield, wt%	Catalyst A			Catalyst B			
W/F, Min.	0.51	0.62	0.94	0.44	0.51	0.63	0.94
Hydrogen	0.018	0.021	0.041	0.025	0.025	0.033	0.046
Dry gas	0.44	0.56	1.14	0.59	0.64	0.86	1.46
LPG	7.33	8.82	13.61	6.18	6.97	10.09	12.34
Gasoline	19.32	23.43	30.78	17.20	20.50	25.03	30.94
TCO	40.09	41.53	37.79	36.33	37.97	39.94	37.67
Bottom (370°C+)	31.81	24.52	14.25	38.73	32.82	22.80	14.92
Coke	0.99	1.13	2.39	0.95	1.08	1.25	2.61
-216°C Conversion	40.17	47.50	62.45	34.96	40.34	49.98	60.99
-370°C Conversion	68.19	75.48	85.75	61.27	67.18	77.20	85.08

Example-2**Effect of reaction temperature on middle distillate yields at same conversion**

This example illustrates the effect of reaction temperature on the yield of middle distillate at a given -216°C conversion. The experiments were conducted in the modified MAT reactor with the same feed as mentioned in Example-1, at two different temperatures, viz., 425°C and 495°C. Catalyst employed here is catalyst C which is commercially available FCC catalyst of following properties as shown in the Table – 8.

Table – 8

		Catalyst – C
Surface Area, m ² /gm	Fresh	172
	Steamed	119
Pore volume, cc/gm		0.32
Crystallinity, %	Fresh	13.80
	Steamed	10.20
UCS °A	Fresh	24.55
	Steamed	24.31

Chemical Analysis, wt%	
RE ₂ O ₃	0.69
Al ₂ O ₃	36.40
Na ₂ O	0.11
Particle size, micron / wt%	
-20 / -40 / -60 / -80 / -105 / -120	3 / 16 / 32 / 56 / 77 / 86
APS, micron	76

Table – 9

Temperature, °C	425		495	
-216°C conversion, wt%	30	50	30	50
W/F, Min.	1.1	2.7	0.10	0.5
Yield Pattern, wt%				
Dry gas	0.20	0.42	0.38	0.56
LPG	4.10	9.1	5.07	10.72
Gasoline	14.94	23.52	16.00	24.58
Heavy naphtha	9.50	14.27	7.11	11.20
LCO	28.68	32.00	25.80	24.50
TCO	38.18	46.27	32.91	35.70
Bottom (370°C+)	41.32	18.00	44.20	25.40
Coke	1.26	2.69	1.44	2.94
370 °C Conversion	58.68	82.00	55.80	74.60
TCO /Rest	1.86	1.29	1.43	0.92

The conversion was varied by changing W/F ratio. The product yields are compared at the same -216°C conversion but at different temperatures. It is noted from Table-9 that at higher temperature, TCO yield and more importantly the TCO/Rest ratio (the ratio of TCO yield and yield of other products e.g., [D]dry gas, LPG, [G]gasoline and [C]coke except bottom and TCO) are much lower in the case of higher reaction temperature. For example, at a given -216°C conversion, TCO yield at 425°C temperature is about 6 - 10% higher than that at 495°C. The

other significant point is that at a low temperature of 425°C , it has been possible to get 46% TCO yield (per pass) at 50% -216°C conversion. Similarly, there is a significant improvement in TCO/Rest ratio for 425°C as compared to that of 495°C at same conversion. This clearly demonstrates that in order to conserve middle distillate range molecules, low reaction temperature is [essential] a desirable parameter.

Example-3

First stage riser cracking conditions

This example illustrates the significance of first stage riser cracking conditions, e.g., temperature, catalyst/oil ratio and conversion, on the yield of middle distillate and other products while employing commercially available FCC catalysts A and C, properties of which are described in Example-1 & 2 respectively. The tests were conducted in modified fixed bed MAT unit with same feed as described in Example-1. Yield data were generated at different conversion level for the catalysts as indicated above and the yields of different products were obtained. TCO/Rest ratios at different conversion levels are plotted in Figure-3, from which it is observed that for both the catalysts, the TCO/Rest ratio increases as the -370°C conversion is reduced. Therefore, it is important to note that the per pass -370°C conversion in the first stage riser should be kept below about 45% and preferably below 40%.

From Figure-3, it is also observed that the TCO/Rest ratio is a strong function of the reactor temperature for a given conversion and catalyst. For example, with catalyst C, while reducing reaction temperature from 490 to 425°C , the TCO/Rest ratio is increased from 3.4 to 3.75 at about -370°C conversion level of 40%. This clearly shows that for the first stage cracking, the reaction temperature should be kept lower, preferably in the range of about $425 - 450^{\circ}\text{C}$.

Example - 4**Catalyst characteristics for middle distillate maximization**

One of the important observations as illustrated in Example-3, is that for maximization of middle distillate yield, it is [necessary]desirable to restrict the per-pass conversion to within about 40 – 45%, and to operate the first stage riser at lower reaction temperature. In this example, we illustrate the importance of catalyst characteristics to obtain higher yield of middle distillate out of the dual/ multi – stage risers.

MAT activity is measured in ASTM MAT units using a standard feedstock and defined as the wt% of products boiling below 216°C including coke at ASTM conditions. All other experiments were conducted at [the]a temperature of 425°C in the modified MAT reactor with the same feed as described in Example-1 and different catalysts. The important properties of the catalysts and the yield / conversion data are compared in Table-10.

Table-10

	Catalyst – A	Catalyst-C	Catalyst-D	Catalyst-E
Surface Area, m ² /gm	103	119	110	20
Zeolite Area, m ² /gm	59	80	62	-
Rare earth content, wt%	1.44	0.69	1.40	-
Matrix Area, m ² /gm	44	39	48	-
Zeolite / Matrix ratio	1.34	2.05	1.29	-
MAT Activity	71.38	74.02	70.19	13.55
TCO Yield at 40% -370°C Conversion	31.00	32.01	30.90	31.20
TCO yield/Rest ratio at 40% -370°C conversion	3.44	4.00	3.39	3.30
W/F for 40% -370°C conversion	0.22	0.25	0.22	3.5

Table -11

	Catalyst-A	Catalyst-C	Catalyst-D
TCO Yield at 80% -370 ⁰ C Conversion	38.45	34.78	43.0
TCO yield/Rest ratio at 80% -370 ⁰ C conversion	0.95	0.80	1.08

It is seen that the zeolite/matrix ratio, TCO yields at 40% -370⁰C conversion, TCO / Rest ratio are in the order of C > A > D. In catalyst C, the available active matrix is adequate to crack the large molecules which are crackable under the prevailing operating conditions but it requires slightly higher W/F ratio. Higher zeolite quantity (proportion) is also synergistically taking part in the over all cracking activity but the conversion of middle distillate to lighter products is not increasing corresponding to higher zeolite content due to lower temperature. However for catalyst-E, whose activity is extremely low, at 40% of -370⁰C conversion, both TCO yield and TCO/Rest ratio is comparable to those with the higher active catalysts. But W/F ratio required to achieve 40% -370⁰C conversion is much higher which is difficult to achieve. At comparable W/F ratio, -370⁰C conversion will be very low, producing very low amount of TCO. Therefore, such low active catalyst is not useful for producing maximum distillate.

Experiments with catalysts A, C & D at a reaction temperature of 495⁰C corresponding to the second riser conditions were taken and the TCO yield and TCO/ Rest ratio are compared at -370⁰C conversion of 80% in Table-11. Both the TCO yield and TCO/ Rest ratio are found to be in the order of D > A > C. It may be noted that the zeolite / matrix ratio is just in the reverse order i.e., C > A > D. The higher quantity of zeolite as well as the high zeolite/matrix ratio in catalyst C, is resulting in overcracking of middle distillate range molecules into lighter products. For a given -370⁰C conversion, the -216⁰C conversion is much higher for catalyst C. It is quite clear that the catalyst which is supposed to be the best in the first riser conditions, may not be that much good for the second riser conditions as far as TCO maximization is concerned. This demonstrates that in order to achieve maximum TCO and minimum Bottom yield, some optimization of the catalyst properties is essential.

[Example – 5**Impact of basic nitrogen compound on middle distillate yield**

It is generally conceived that low activity of the catalyst is desirable for maximum distillate yield. Basic nitrogen compounds present in feed stock interact with the catalyst at reaction conditions leading to loss of the active acid sites and hence decrease of catalyst activity. Two feed stocks were prepared containing 200 and 700 PPM pyridine respectively. The experiments were conducted in the modified MAT reactor with catalyst C using the same feed stock as mentioned in Exmpl-1, but containing different PPM of pyridine, at the temperature of 425°C. The conversion and yield data are shown in Table-12.

Table-12

	Feed without Pyridine	Feed containing 200 PPM Pyridine	Feed containing 700 PPM Pyridine
-216°C conversion at 40% -370°C conversion	13.50	14.15	13.99
TCO Yield at 40% -370°C conversion	32.00	30.90	29.98
TCO/Rest ratio at 40% -370°C conversion	4.00	3.39	3.00
W/F to achieve 40% -370°C conversion	0.25	0.30	0.38

It is observed that both TCO and TCO/Rest ratio are decreasing as the feed basic nitrogen content is increasing. However, at 40% -370°C conversion, -216°C conversion is increasing with increase in basic nitrogen in feed upto 200 PPM after which it reduces marginally at 700 PPM of pyridine in feed. This is due to the irreversible adsorption of the nitrogenous basic compounds leading to preferential destruction/poisoning of the strong acid sites, which are responsible for heavy molecule cracking. This is reflected in the higher W/F requirement to achieve 40% -370°C conversion. However, so called relatively weaker acid sites which do not get affected by basic nitrogen helps in cracking of middle distillate range molecules at higher W/F resulting higher -216°C conversion. In case of 700 PPM pyridine containing feed, even some of the relatively weaker acid sites are getting affected reducing both -216°C and -370°C conversion as compared to the 200 PPM pyridine containing feed case. This example demonstrates that just activity reduction may not lead to higher middle distillate yield.]

Example – [6] 5**Impact of cracking conditions for second stage riser operation**

This example illustrates the significance of second stage riser cracking conditions e.g., temperature, catalyst/oil ratio and conversion on the yield of middle distillate. The tests were conducted in modified fixed bed MAT unit as described in Example-1, using catalyst C, at the temperature of 425, 490 and 510°C. The feed stock used is 370°C⁺ product obtained from first stage cracking in circulating riser FCC pilot plant, the properties of which is summarized in Table-13. Product yields data were generated at different conversion levels at different temperatures for catalyst C and according the TCO/Rest ratios at different conversion levels are plotted in Figure-4.

Table – [13] 12

Density, gm/cc @ 15°C	0.903
CCR, wt%	0.43
Sulfur, wt%	1.75
Olefins, wt%	Nil
Saturates, wt%	59.0
Aromatics, wt%	41.0

From the Figure-4, it is observed that at a given temperature, the TCO/Rest ratio increases as the -370°C conversion reduces. Also, at a given -370°C conversion, TCO/Rest ratio improves as the reaction temperature reduces. For example, at about -370°C conversion of about 55%, TCO/Rest ratio increases from 1.22 to 1.34 as the temperature is reduced from 510 to 490°C. This clearly shows that even for the second stage cracking, the reaction temperature should be kept preferably lower. However, it will also lead to generation of higher quantity of bottom at same W/F ratio. At 425°C, W/F required to crack the 370°C⁺ product from first stage cracking along with the recycle stream (unconverted part from the second riser) will be very high and hence difficult to achieve. Another important fact is that the mean average boiling point (MeABP) of second riser combined feed is definitely higher than that of first riser. Operation at lower temperature than the MeABP of the second riser combined feed is not desirable as it will

lead to non-selective thermal cracking of the non-vaporized feed producing higher quantity of Coke and Dry gas. Considering these, it has been established that in the second riser, the reaction temperature should be preferably kept in the range of 460 - 510°C.

Example – [7] 6

Combined effect of two stage cracking on middle distillate yield

In this example, the yields from two stage catalytic cracking for maximization of middle distillate is demonstrated. The experiments have been conducted using catalyst C in continuously circulating fluid bed pilot plant of feed rate 0.75 kg/hr where both the riser and regenerator are operated isothermally. The feed is the same as mentioned in Example-1. After first stage cracking at 425°C, the product is separated into 370°C– and 370°C+ fractions. In the second stage, the 370°C+ fraction is cracked at 495°C using the same catalyst as used in the first stage. The product yields from the first and second stage cracking and also the combined yields are given in Table-13.

Table-[14] 13

	first stage	second stage	Combined yields
Temperature, °C	425	495	
<u>Yield Pattern, wt%</u>			
Dry gas	0.26	1.28	0.81
LPG	3.37	16.65	10.55
Gasoline	10.65	26.03	21.88
Heavy naphtha	8.54	13.31	14.28
LCO	32.33	19.47	40.73
TCO	40.87	32.78	55.01
370 °C +	43.25	20.44	8.82
Coke	1.70	2.85	2.93

It is clearly seen that the ratio of yield of TCO and the sum of yields of [D]dry gas, LPG, [G]gasoline and [C]coke (TCO/Rest) is very high in case of the first stage cracking, which is

essentially contributing higher TCO yield for the overall process. For second stage cracking, the TCO/Rest ratio is similar to that of conventional distillate mode FCC unit as the severity required for minimizing the bottom yield is high enough to crack significant portion of TCO produced from heavy molecule cracking.

The yield comparison between single and dual riser cracking at similar -216°C conversion with same catalyst and feed is compared in Table-14. It is seen that for same -216°C conversion, -370°C conversion is much higher resulting about 20% higher yield of TCO in case of two stage cracking. This establishes the workability of the concept of the present invention where process schemes, catalyst and operating conditions are such that TCO over-cracking is restricted with simultaneous upgradation of heavy molecules to TCO range molecules. Here, the first riser operates to extract as much TCO as possible while minimizing the yields of lighter products and the second riser is operated to upgrade as much bottom as possible while maximizing the yield of TCO. This process overcomes the trade off between lower bottom yield and higher TCO yield.

Table-[15] 14

	Dual riser	Single riser
Temperature, $^{\circ}\text{C}$	425 & 495	495
Yield Pattern, wt%		
Dry gas	0.81	0.56
LPG	10.55	10.72
Gasoline	21.88	24.58
Heavy naphtha	14.28	11.20
LCO	40.73	24.50
TCO	55.01	35.70
370°C^{+}	8.82	25.40
Coke	2.93	2.94
-216 conversion, wt%	50.45	50.0

Example – [8] 7**Comparison of Micro-reactor & Circulating pilot plant data**

This example shows the comparison of individual product yields obtained from Micro-reactor and circulating Pilot Plant using the same catalyst and feedstock at a similar -216°C conversion range. From the data summarized in Table-16, it is noticed that at similar conversion, there is an excellent match in [G]gasoline, TCO and bottom yields. The main difference is coming in the yields of [D]dry gas, LPG and [C]coke. This is mainly due to the non-selective thermal cracking reactions occurring at the riser bottom as well as at the end of the riser in the pilot plant. This has resulted in relatively higher yield of [D]dry gas and [C]coke in the pilot plant riser. This example demonstrates that so far as the yields of TCO and un-reacted bottom are concerned, the inferences drawn based on either Micro-reactor or Pilot Plant data are going to be same.

Table-[16] 15

	Pilot Plant data		Micro-reactor data	
Feed rate, gm/min	12.9	13.3	-	-
CCR, gm/min	55.5	53.0	-	-
Cat/Oil (w/w)	4.29	3.98	-	-
W/F, min.	-	-	0.609	0.501
Contact time, sec	-	-	30	30
-216 Conversion, wt%	29.86	25.0	29.39	24.93
<u>Product Yields, wt%</u>				
Dry gas	0.62	0.36	0.17	0.13
LPG	8.28	6.29	9.96	8.61
Gasoline	11.82	10.7	12.00	10.65
Heavy Naphtha	7.15	5.92	5.80	4.62
LCO	27.3	26	28.29	26.61
TCO	34.45	31.9	34.09	31.23
370°C +	42.82	49	42.31	48.46
Coke	2.00	1.71	1.46	0.91

Example – [9] 8**Comparison of the yields of present two stage process in present invention, commercial FCCU and two stage hydrocracker**

The product yields of the present invention [is]are compared with that of commercial distillate mode FCC and two-stage hydrocracker units in Table-17. The data for the process of the present invention is the combined yield obtained from two stage cracking where the two risers are operated at 425°C and 495°C, respectively.

Table – [17] 16

Product yields, wt% of feed	Distillate mode FCC	Present process	Yields, wt% of feed	Distillate mode Hydrocracker	Present process
Dry gas	2.50	0.78	Dry gas	1.74	0.70
LPG	10.5	10.55	LPG	2.91	9.11
Gasoline (C ₅ -150°C)	27.5	21.88	Gasoline (C ₅ -120°C)	16.28	12.86
Heavy Naphtha a (150-216°C)	12.5	14.28	(120-216°C) (120-285°C)	- 27.91	18.41 -
LCO (216-370°C)	30.0	40.73	(216-390°C)	-	50.39 -
TCO (150-370°C)	42.5	55.01	(120-390°C)	73.26	68.80
370°C ⁺	12.75	8.82	390°C ⁺	5.81	5.85
Coke	4.25	2.93	Coke	-	2.68
-216°C conv.	57.25	50.45	-216°C conv.	-	-
-370°C conv.	87.25	91.18	-390°C conv.	94.19	94.15

It is observed that in the process of the present invention, the TCO yield is higher by about 12.50% as compared to the yield from a commercial FCC unit. By varying the cut point of TCO from 150 - 370°C to 120 – 390°C as reported for the [H]hydrocracker unit, and processing

the hydrocarbon product fraction from the first riser having boiling points greater than or equal to 390°C in the second riser, the yield of TCO increases by about 14 wt% which is only about 5% less than that from the commercial [H] hydrocracker unit. Also, the conversion of hydrocarbon products having boiling points less than or equal to 390°C (-390°C conversion) is similar to what is achievable in a [H]hydrocracker and -370°C conversion is better than the distillate mode FCC unit. This demonstrates that, without using external hydrogen and operating under very high pressure, it is possible to produce higher yields of middle distillate product which [is]are close to that from a distillate mode two stage [H]hydrocracker unit.

Example –[10] 9

Comparison of properties of TCO obtained in the process of the present invention with middle distillate products obtained from commercial FCCU and two stage Hydrocracker

The properties of the TCO obtained from the process of the present invention is compared with TCO from commercial distillate mode FCC and Diesel from distillate mode two stage Hydrocracker units which is given in Table-17.

Table –[18] 17

	Process of the present invention		Distillate mode FCC	Distillate mode Hydrocracker
	1	2	3	4
	TCO	Middle distillate	TCO	Diesel
TBP cut point, °C	150 - 370	120 - 390	150 - 370	150 - 390
Density @ 15°C, gm/cc	0.8793	0.8863	0.8654	0.835
Pour point, °C	0.7	36	0 – 2	6 – 10
Kinematic Viscosity @ 50°C, CST	2.20	7.00	2.7	9.0
PONA Analysis, wt%				
Olefins	19.97	6.82	18.6	Nil
Saturates	24.64	49.26	22.1	91
Aromatics	55.39	43.92	59.3	9
Cetane no.	36.22	38.39	28 - 30	63

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SUBSTITUTE SPECIFICATION

A MULTI STAGE SELECTIVE CATALYTIC CRACKING PROCESS AND A SYSTEM FOR PRODUCING HIGH YIELD OF MIDDLE DISTILLATE PRODUCTS FROM HEAVY HYDROCARBON FEEDSTOCKS

Field Of The Invention

This invention relates to a process and a system for the improved production of middle distillate products comprising hydrocarbons having carbon atoms in the range of C_8 to C_{24} in high yield, from heavier petroleum fractions through multistage catalytic cracking of varying severity levels with solid acidic catalyst without using external hydrogen.

Background Of The Invention

Conventionally, middle distillate range products, e.g. heavy naphtha, kerosene, jet fuel, diesel oil and light cycle oil (LCO), are produced in petroleum refineries by atmospheric/vacuum distillation of petroleum crude and also by the secondary processing of vacuum gas oil and residues or mixtures thereof. Most commonly practiced commercial secondary processes are Fluid Catalytic Cracking (FCC) and Hydrocracking. Hydrocracking employs porous acidic catalysts similar to those used in catalytic cracking but associated with hydrogenation components such as metals of Groups VI and VII of the Periodic Table to produce good quality of middle distillate products in the boiling range of C_8 - C_{24} hydrocarbons. An excess of hydrogen is supplied to the hydrocracking reactor under very high pressure (150-200 atm.) and at a relatively lower temperature (375-425°C) in fixed bed reactors with two phase flow. Due to severe hydrogenation, all hydrocarbon products from Hydrocracker are highly saturated with low sulfur and aromaticity. The yield of middle distillate hydrocarbons (126-391°C boiling range) in hydrocracking is typically very high, i.e. up to 65 - 80 wt% of feed.

FCC process, on the other hand, is employed for producing substantial quantities of high octane gasoline and LPG. In countries where demand for middle distillate product is higher, heavy cracked naphtha (HCN: C_8 - C_{12} hydrocarbons) and light cycle oil (LCO: C_{13} - C_{24}

hydrocarbons) production are maximized by manipulating operating variables so as to vary the reaction and regenerator severity levels. U.S. Patent Nos. 3,894,931 and 3,894,933 address such operations. Typically, diesel yield in FCC is maximized by maintaining a lower reaction and regeneration severity and recycling of unconverted residual products. Catalysts with lower zeolite/matrix ratio and MAT (Micro Activity Test) activity of about 60-70 is normally preferred. By proper selection of FCC variables and innovations involving catalyst type and recycle of heavy cycle oil and residual slurry oil, distillate yield can be increased by considerable amount at the expense of Gasoline yield. As the FCC unit operation is shifted from gasoline mode to middle distillate maximization mode, the LCO cetane number increases and thus could be more useful for blending into the diesel pool.

However, while running at low severity operations for maximizing diesel yield, the unconverted bottom yield also increases to a significant extent and sometimes may even exceed 20 wt% of fresh feed, as against 5-6 wt% for the usual gasoline mode operation. The other drawback of low severity operation is in the high amount of recycle oil being fed to the bottom of the riser with fresh feed for further cracking. Firstly, this reduces the throughput of riser reactor and secondly, with a single riser and product fractionator, the recycle is nonselective. Consequently, diesel yield from FCC with a conventional cracking catalyst could be maximized up to 40-45 wt% in spite of running at low reaction severity (495°C riser temperature) and fairly high recycle ratio (30% of fresh feed).

Besides the operation of conventional FCC in middle distillate maximization mode, there are several other processes aiming for improvement in middle distillate yield. U.S. Pat. No. 5,098,554 discloses a process of fluid catalytic cracking with multiple feed injection points where fresh feed is charged to upper injection points and unconverted slurry oil is recycled to a location below the fresh feed nozzles. Essentially, the process conditions are similar to that of gasoline mode FCC operation (e.g., 527°C riser top temperature) which favors gasoline production. By adopting split feed injection, middle distillate yield is marginally increased at the expense of gasoline yield.

U.S. Pat. No. 4,481,104 describes about an ultra-stable Y-zeolite, of high framework silica to alumina ratio having low acidity and large pores, use of which in catalytic cracking of gas oil, enhances distillate yield. It may be noted that yield of 420 – 650°F fraction is maximize about 28 wt% of feed and, as 650°F- conversion increases beyond 67 wt%, the yield of 420– 650°F fraction reduces. Therefore, as discussed earlier, yield of the distillate is relatively higher only at the higher yield of unconverted fraction.

Yet another process, reported in U.S. Pat. No. 4,606,810, discloses a scheme of two riser cracking for improving total gasoline plus distillate yield. Here, the feed is first cracked in the first riser with spent catalyst from the second riser and the unconverted part is further cracked in a second riser in presence of regenerated catalyst. The basic operation is of high severity producing maximum amount of gasoline and the yield of LFO is around 15 – 20 wt% of feed. It may also be noted that while increase in gasoline yield is in the range of 7.5 – 8.0 wt%, increase in LFO yield is merely in the range of 1.5 – 3.0 wt% on fresh feed basis.

Two stage processing of hydrocarbon feedstock has been employed by different researchers in the field of catalytic cracking. Several processes have been developed in which first stage processing removes metals and Conradson Carbon Residue (CCR) impurities from feed using a low activity cheap contact material with abundant surface area. The demetallized feed is then processed in a more conventional second stage reactor under high severity conditions to maximize the conversion and gasoline production. U.S. Pat. No. 4,436,613 describes such a process of two stage catalytic cracking using two different types of catalyst. In the first stage, the CCR materials and metals are separated from the rest of the feedstock along with mild cracking over a relatively lower activity catalyst. The residual un-cracked product of the first stage is then contacted with a high activity catalyst under higher reaction severity for gasoline maximization. It may be noted that in this process, two dedicated strippers and regenerators are used to avoid the mixing of two different types of catalysts.

Dual riser high severity catalytic cracking process described in U.S. Pat. No. 3,928,172 utilizes a mixture of large pore REY zeolite catalyst and a shape selective zeolite catalyst where gas oil is cracked in the first riser in the presence of the aforesaid catalyst mixture. The heavy

naphtha product from the first riser and/or virgin straight run naphtha are cracked in the second riser in the presence of catalyst mixture to produce high octane gasoline together with C₃ and C₄ olefins. U.S. Pat. No. 4,830,728 discloses a process for upgrading straight run naphtha, catalytically cracked naphtha and mixtures thereof in a multiple fluid catalytic cracking operation utilizing mixture of amorphous cracking catalyst and/or large pore Y-zeolite based catalyst and shape selective ZSM-5 zeolite catalyst to produce high octane gasoline.

U.S. Pat. No. 5,401,387 describes a process of multistage catalytic cracking where the first stage cracks a first feed over a shape selective zeolite to produce lighter products rich in iso-compounds which may be used for making ethers. A second feed, which may include 700°F+ liquid from first stage, is cracked in the second stage. Another process, as described in U.S. Pat. No. 5,824,208, discloses a scheme in which hydrocarbon is initially contacted with cracking catalyst forming a first cracked product which, after recovering of the product fraction having boiling point of more than 430°F, is subjected to cracking in a second riser. The basic objective of this invention is to maximize the yield of light olefins and minimize the formation of aromatic compounds by avoiding undesirable hydrogen transfer reactions.

So far, most of the prior art methods have concentrated on multiple riser catalytic cracking for maximization of gasoline yield and its octane numbers, increased yield of iso-olefin for production of ethers, increased yield of light olefins, etc. From the prior art information and also from our experience of operating low severity FCC units, it is quite clear that maximizing middle distillate yield in FCC (without using external hydrogen) is not achieved beyond a level of 40-45 wt% of fresh feed. Further, persons involved in fluid catalytic cracking would be aware that middle distillate, being an intermediate product in the complex catalytic cracking reactions, is very difficult to maximize because, when the severity is increased, it is over cracked to lighter hydrocarbons.

Objects

Accordingly, one object of the present invention aims to propose a novel catalytic cracking process for producing middle distillate products in very high yield (about 50-65 wt%).

- i) contacting preheated feed with a mixed catalyst in a first riser reactor, under catalytic cracking conditions including catalyst to oil ratio of about 2 to 8, WHSV of about 150-350 hr⁻¹, contact period of about 1 to 8 seconds and temperature in the range of about 400°C to 500°C, to obtain first cracked hydrocarbon products;
- ii) separating the first cracked hydrocarbon products from the first riser reactor into a first fraction comprising hydrocarbons with boiling points less than or equal to about 370°C and a second fraction comprising hydrocarbons with boiling points greater than or equal to 370°C that comprise unconverted feed material;
- iii) cracking the second fraction from the first riser reactor, comprising hydrocarbons having boiling points greater than or equal to 370°C, in the presence of regenerated catalyst, in a second riser reactor operating under catalytic cracking conditions, including WHSV of about 75-275 hr⁻¹, catalyst to oil ratio of about 4-12 and riser top temperature of about 425 - 525°C to obtain second cracked hydrocarbon products;
- iv) separating the catalytically cracked products from the second riser reactor, alongwith cracked products comprising hydrocarbons having boiling points less than equal to 370°C, from the first riser reactor, in a main fractionating column to yield cracked products comprising dry gas, LPG, gasoline, middle distillates, heavy cycle oil and slurry oil;
- v) recycling the entire heavy cycle oil, comprising hydrocarbons having boiling points in the range of about 370°C to 450°C, and full or part of the slurry oil, having boiling points greater than or equal to about 450°C, into the second riser reactor at a vertically displaced position lower than the position of introduction of the main feed, comprising a bottom fraction comprising an unconverted hydrocarbon fraction, having boiling points greater than or equal to about 370°C, from the first riser reactor to obtain middle distillate products comprising hydrocarbons having carbon atoms in the range of about C₈ - C₂₄ ranging from about 50 to 65 wt % of the fresh feed into the first riser.
- iv) Optionally, recycling the fraction of unconverted hydrocarbons with boiling points greater than or equal to about 370°C, obtained in step (v), in riser reactor(s)

by repeating steps (iii) to (iv), to obtain substantially pure middle distillate products.

In an embodiment, the feed stock is selected from petroleum based heavy feed stock, such as vacuum gas oil (VGO), visbreaker/cooker heavy gas oil, cooker fuel oil, hydrocracker bottoms, etc.

In another embodiment, mixed catalyst is obtained from an intermediate vessel used for mixing the spent catalyst from the common stripper, or preferably from a first stripper, with the regenerated catalyst from the common regenerator and charging the mixed catalyst, with coke content in the range of about 0.2 to 0.8 wt% to the bottom of the first riser at a temperature of 450 - 575°C.

In another embodiment, the exit hydrocarbon vapors from the first and second risers are quickly separated from respective spent catalysts using respective cyclones and/or other conventional separating devices to minimize the overcracking of middle distillate range products into less desirable lighter hydrocarbons.

In yet another embodiment, the spent catalysts from the first and second riser reactors are passed through respective dedicated catalyst strippers or a common stripper to render the catalysts substantially free of entrained hydrocarbons.

In a further embodiment, the regenerated catalyst with coke content of less than 0.4 wt% is obtained by burning a portion of the spent catalyst from the first stripper, the spent catalyst from the second stripper or the common stripper in a turbulent or fast fluidized bed regenerator in the presence of air or oxygen containing gases at a temperature ranging from about 600°C to 750°C.

In another embodiment, the catalyst circulation between the fluidized bed riser reactors, strippers and the common regenerator is continuously through standpipe and slide valves.

In yet another embodiment, the critical catalytic cracking conditions in the first reactor, including mixed regenerated catalyst, result in very high selectivity of middle distillate range products and conversion of hydrocarbon products of boiling point less than or equal to 370°C at lower than 50 wt% of the fresh feed.

In another embodiment, the zeolite cracking catalyst comprises commercial ReUSY zeolite based catalyst, having a fresh surface area of about 110-180 m²/gm., a pore volume of about 0.25-0.38 cc/gm and an average particle size of about 60-70 microns, along with selective acidic bottom upgrading components in the range of 0-10 wt%.

In still another embodiment, the unconverted heavy hydrocarbon fraction from the second riser, that is being recycled into the second riser, ranges from about 0-50 wt% of the main feed rate (i.e. 370°C+ fraction) from the first riser to the second riser, depending on the nature of the feedstock and operating conditions kept in the risers.

In yet another embodiment, the amount of steam used for feed dispersion and atomization in the first and the second riser reactors is in the range of about 1-20 wt% of the respective total hydrocarbon feed depending on the quality of the feedstock.

In further embodiment, the spent catalyst resides in the stripper for a period of up to 30 seconds.

In another embodiment, the pressures in the first and second riser reactors are in the range of 1.0 to 4.0 kg/cm²(g).

In yet another embodiment, the regenerated catalyst entering at the bottom of the second riser reactor has coke of about 0.1-0.3 wt%, is at a temperature of about 600-750°C, and is lifted by catalytically inert gases.

In a further embodiment, the combined total cycle oil (150-370°C) product, which is a mixture of heavy naphtha (150-216°C) and light cycle oil (216- 370°C), has a higher cetane number than that from conventional distillate mode FCC unit and other properties, such as specific gravity, viscosity, pour point, etc. that are in the same range as of the similar boiling range products of a commercial distillate mode FCC unit.

In still another embodiment, by changing the cut point of the TCO from the first riser to 120-370°C, processing 370°C+ part of the first riser product in the second riser, and changing the cut point of TCO from second riser to 120-390°C, the yield of overall combined TCO product increases by 8-10 wt% and the combined TCO product has substantially the same properties, but improved cetane number, as that of TCO from commercial distillate mode FCC unit.

Brief description of the accompanying drawings:

The invention is illustrated hereinbelow with reference to the following accompanying drawings, wherein:

Fig.1 shows a conventional fluid catalytic cracking single riser system.

Fig.2 shows a fluidized catalytic cracking two riser system of the present invention.

Fig.3 is a graph showing the ratio of TCO Yield/Yields of (rygas+LPG+asoline+oke) Vs. -370°C conversion with first riser feed at two different temperatures (425°C & 490°C).

Fig.4 is a graph showing the ratio of TCO Yield/Yields of (dry gas+LPG+gasoline+coke) Vs. -370°C conversion with second riser feed at two different temperatures (490°C & 510°C).

The reference numbers of the several figures of the drawing are unique to each figure.

Description of Fig.1 :

In the conventional Fluid Catalytic Cracking (FCC) unit, fresh feed (1) is injected at the bottom of the riser (2) whereupon it comes into contact with hot regenerated catalyst from the regenerator (3). The catalyst along with hydrocarbon feed and product vapors ascends the riser and at the end of the riser spent catalyst is separated from the hydrocarbon vapor and subjected

to steam stripping. The hydrocarbon vapors from the riser reactor are sent to a main fractionator column (4) for separating into the desired products. The stripped catalyst is passed to a regenerator (3) where the coke deposited on the catalyst is burnt off and the clean hot catalyst is circulated back to the bottom of the riser.

The fluidized catalytic cracking two riser system of the invention is schematically shown in Fig.2, and described in detail hereinbelow.

The fluidized bed (sometimes referred to as a transport bed) catalytic cracking system for the production of high yield of middle distillate products, comprising hydrocarbons having numbers of carbon atoms in the range of about C_8 to C_{24} , from heavy petroleum feeds, comprises at least two riser reactors (1 and 2). A fresh feed is introduced into the first riser reactor (1), typically at the bottom section but above regenerated catalyst entry zone through a feed nozzle (3). At the end of the first riser reactor (1), the spent catalyst is quickly separated from hydrocarbon product vapors, using separating devices (4), and the separated catalyst is subjected to multistage steam stripping to remove any entrained hydrocarbons. A conduit (5) feeds a part of the said stripped catalyst into a regenerating apparatus (7) and another part of the stripped catalyst from the conduit (5) travels through another conduit (6) into a mixing vessel (10). Thereafter, the mixed catalyst from the mixing vessel (10) travels through a conduit (19) and is fed to the bottom of the first riser reactor (1). The hydrocarbon product vapors from the first riser reactor (1), which are separated from the catalyst in the separating devices (4), are fed to a vacuum or atmospheric distillation column (13) through conduit (12) whereby the first cracked hydrocarbon products are separated into a first fraction, comprising hydrocarbons having boiling points less than or equal to 370°C , and a second fraction, comprising hydrocarbons with boiling points greater than or equal to 370°C which includes uncracked hydrocarbons. The said second fraction, comprising uncracked hydrocarbon products, is fed through feed nozzle (16) into the bottom of a second riser reactor (2) above the regenerated catalyst entry zone, and the regenerated catalyst from the regenerating apparatus (7) is fed to the bottom of the second riser reactor (2) through a conduit (9). Subsequently, the hydrocarbon products of the second riser reactor (2) are separated from the catalyst, in separating devices (11), and the cracked products of the second riser reactor (2), along with the products of the first fraction of the first riser reactor

(1) comprising hydrocarbons with boiling points less than or equal to 370°C, are fed to a main fractionator column (15) that conventionally separates the said products into dry gas, LPG, gasoline, heavy naphtha, light cycle oil, heavy cycle oil, and slurry oil. The entire heavy cycle oil and all or part of the slurry oil, consisting mainly of hydrocarbons with boiling points greater than or equal to 370°C, are recycled back to the second riser reactor (2) through a separate feed nozzle (17) located at a point lower than the position of introduction of main feed. The feed and cracked product vapors travel along with the catalyst, through the riser reactor whereupon the spent catalyst is separated from product vapors of the second riser reactor (2) in separating devices (11), and the spent catalyst is subjected to multistage steam stripping for removal of entrained hydrocarbons. The stripped catalyst travels through a conduit (18) into the regenerating apparatus (7), wherein the coke on catalyst is burnt in the presence of air and/or oxygen containing gases at high temperature, and the flue gas from regeneration is separated from the entrained catalyst fines in separating devices (20) and the flue gas leaves from top of the regenerating apparatus (7) through a conduit (21) for heat recovery and venting through stack. The hot regenerated catalyst is withdrawn from the regenerating apparatus (7) and divided into two parts, one going to the mixing vessel (10) through the conduit (8) and the other directly to the bottom of the second riser reactor (2). The mixed catalyst from the mixing vessel (10) is fed through the conduit (19) to the inlet of the first riser reactor (1). The level of the catalyst bed is controlled in the individual or common stripper. The catalyst circulation rate from the common regenerator and the quantity of the spent and regenerated catalyst entering into the mixing vessel (10) is controlled using slide valves placed in the conduits and thereby producing high yield of middle distillate products.

At the bottom 'Y' section of both the risers (1 & 2), steam is used to lift the catalyst in upward direction up to the feed entry zone. Also steam is used in the feed nozzles (3, 16 & 17) for atomization and dispersion of the feed. The quantity of the steam flow into the respective risers (1&2) is varied depending on the feedstock quality and the desired velocity in the risers.

As an example, a system designed to practice the process of the invention has been described employing only two riser reactors. It is pertinent to note that in practice, riser reactors of any desired number may be functionally attached downstream of the second riser reactor so

that the unconverted hydrocarbons obtained from the second riser may be further treated in accordance with the process described hereinabove and eventually, substantially pure middle distillate products may be obtained in high yield from the original feed.

In catalytic cracking processes using zeolite based catalyst, the reactions proceed sequentially. Middle distillate yield can be increased, if cracking thereof to lighter products is restricted. Any attempt in this regard is likely to reduce the conversion, resulting in higher yield of unconverted products. Conventionally, recycling of unconverted fraction has been practiced to improve the overall conversion. The severity required for cracking of the unconverted recycled fraction is adequate to produce significant quantity of gasoline and LPG by over-cracking of middle distillate range product. It also promotes hydrogen transfer reactions producing aromatics in middle distillate range products and therefore, deteriorates the cetane quality. To summarize, it may be noted that maximization of intermediate product middle distillate by a cracking reaction is more challenging as compared to maximization of gasoline.

In distinction to other prior art processes, the present invention provides a process for producing maximized quantity middle distillate through catalytic cracking of heavy hydrocarbon fractions employing multiple risers. The applicants realized that the middle distillate selectivity is higher only at lower conversion. In fact, the ratio of yield of total cycle oil (TCO:150-370°C) to the sum of other products, (such as, dry gas, LPG, gasoline and coke) increases as the conversion reduces. Moreover, riser temperature has dramatic impact on the selectivity. At same conversion, the applicants have found that middle distillate selectivity improves significantly as riser temperature is reduced. The applicants have also investigated the role of coke on regenerated catalyst (CRC) and discovered that there is an optimum CRC for maximum yield of TCO (Ref.: Ind. Chem. Res., 32, 1081, 1993). Finally, the applicants have arrived at some specific conditions (comprising lower riser temperature, low contact time, low catalyst oil ratio, higher CRC, etc.) and type of the catalyst with which yield of TCO is maximized.

According to the present invention, petroleum feed stocks, such as vacuum gas oil (VGO), coker fuel oil, coker/visbreaker heavy gas oil, hydrocracker bottom, etc., are catalytically cracked in presence of solid zeolite catalyst with or without selective acidic bottom cracking

components in multiple riser-reactors. The feed is first preheated to a temperature in the range of about 150-350°C and then injected into a pneumatic flow, riser type cracking reactor with a residence time of about 1-8 seconds, and preferably of about 2-5 seconds. At the exit of the riser, hydrocarbon vapors are quickly separated from catalyst for minimizing the over cracking of middle distillate to lighter products.

The product from the first riser is separated in a fractionator into at least two streams, one comprising hydrocarbons having boiling points below about 370°C and the other comprising hydrocarbons having boiling points greater than about 370°C. The removal of hydrocarbon products having boiling points less than or equal to about 370°C reduces the chance of over-cracking of middle distillate range molecules to lighter products. The fraction, comprising hydrocarbons, including unconverted hydrocarbons, having boiling points greater than or equal to about 370°C, from the first riser is pre-heated and then injected to the second riser reactor with residence time of about 1-12 seconds, and preferably in the range of about 4-10 seconds, through the feed nozzles located at a higher elevation. In the second riser, the regenerated catalyst is contacted with the recycle stream of unconverted heavy hydrocarbons from the second riser at a relatively lower elevation of the riser. This allows preferential cracking of the recycle components under high severity conditions (e.g., higher temperature, higher dynamic activity of the catalyst owing to low coke on regenerated catalysts) at the bottom of second riser. Typically, recycle ratio is maintained in the range of about 0-50% of the feed throughput in the second riser.

Steam and/or water, in the range of 1-20 wt% of feed, is added for dispersion and atomization in both the risers depending on type of feedstock. The desired velocity in the risers, especially in the first riser, is adjusted by the addition of steam.

The hydrocarbon product vapor from the second riser is quickly quenched with water/another, cooler hydrocarbon fraction and separated for minimizing the post riser non-selective cracking. The product from the second riser and the product boiling below about 370°C from the first riser are separated in a common fractionator into several products, such as dry gas, LPG, gasoline, heavy naphtha, light cycle oil and cracked bottoms. Part of the bottom product, including unconverted hydrocarbon feed, (the 370°C+ fraction) from the second fractionator is

recycled to the second riser and a remaining part is sent to rundown after removal of catalyst fines.

The spent catalyst, with entrained hydrocarbons from the riser exit, is then passed through a common or separate stripping section where counter current steam stripping of the catalyst is carried out to remove the hydrocarbon vapors from the spent catalyst. The catalyst residence time in the strippers is required to be kept in the lower side of preferably less than about 30 seconds. This helps to minimize undue thermal cracking reactions and also reduces the possibility of over-cracking of middle distillate range products. Stripped catalyst is then passed to a common dense or turbulent fluidized bed regenerator where the coke on catalyst is burnt in presence of air and/or oxygen containing gases to achieve coke on regenerated catalyst (CRC) of lower than about 0.4 wt% and preferably in the range of about 0.1 - 0.3 wt%. A part of the regenerated catalyst is directly circulated to the second riser reactor via standpipe/slide valve at a temperature of 600 - 750°C.

As mentioned earlier, there is an optimum CRC at which maximum TCO yield is obtained. In order to extract maximum TCO from the first riser, CRC is required to be maintained at relatively higher level, for example in the range of 0.2- 0.8 wt% depending on catalyst and operating conditions. In the second riser, the desirable CRC is relatively lower (for example in the range of 0.1 - 0.3 wt%) in order to utilize the full activity potential of the catalyst. Also, the temperatures of the regenerated catalyst entering into the two risers are different. The lower temperature and higher CRC of the catalyst entering to the first riser is achieved by mixing a part of the stripped catalyst from the first riser/common stripper with regenerated catalyst in a separate vessel equipped with fluidization steam, and circulating the mixed catalyst to the bottom of the first riser via a stand pipe/slide valve. The mixed catalyst enters at the bottom of the first riser with a temperature in the range of about 450 - 575°C (preferably in the range 475 - 550°C) and CRC of lower than about 0.8 wt% (preferably in the range of 0.25 - 0.5 wt% depending on type of catalyst). Another option for controlling the catalyst return temperature in the first riser is to employ a catalyst cooler so that catalyst/oil ratio can be controlled substantially independently. However, the instant mixing vessel is preferred since it acts as second stage stripper and helps to adjust the coke level on the catalyst.

Prior to the injection of the 370°C+ fraction of the first riser product, the fresh regenerated catalyst is contacted with a recycle stream comprising unconverted hydrocarbons from the second riser at a relatively lower elevation of the riser. The recycle components are preferentially cracked at the high severity conditions prevailing in the second riser bottom before the injection of 370°C+ fraction of first riser product. Typically recycle ratio is maintained in the range of about 0 – 50% of the second reactor feed throughput depending on the type of the feed to be processed and the conversion level in both the reactors. If the recycle rate is less, it may be injected along with the main feed i.e., 370°C+ fraction of first riser product.

In the present invention, the first riser operates in the range of about 150 - 350 hr⁻¹ weight hourly space velocity (WHSV), about 2 - 8 catalyst to oil ratio, and about 400 - 500°C riser top temperature to convert the feedstock to selectively cracked product including 35 – 45 wt% min. TCO yield and 40 - 60 wt% 370°C+ (bottom) yield. The second riser operates in the range of about 75 - 275 hr⁻¹ WHSV, about 4 -12 catalyst to oil ratio and about 425 -525°C riser top temperature. The absolute pressures in both reactors are about 1 - 4 kg/cm² (g). Steam and/or water, in the range of about 1 - 20 wt% of feed, is added not only for dispersion and atomization of feed but also to attain the desired fluidization velocity in the risers, especially in the first riser bottom. It also helps in avoiding the coke formation or catalyst agglomeration.

Comparison of major process conditions of the process of the present invention with conventional FCC & multi stage process is shown below :

Table – 1

	Multistage process of the present invention				FCC Process
	first reactor		second reactor		
	Range	Preferred Range	Range	Preferred Range	Range
WHSV, hr ⁻¹	150 – 350	200– 300	75 – 275	120 – 220	125 -200
Catatyst/Oil ratio (w/w)	2 – 8	3 – 5	4 –12	5 – 8	4 - 8

Riser temp., °C	400 – 500	425 - 475	425 – 525	460 – 510	490- 540
Steam injection, wt% of feed	1 - 20	8 - 12	1 – 20	4 – 8	0 - 10

Use of multiple riser concepts is not new, as each researcher has employed it for different purposes. The present invention utilizes dual or multiple riser systems for the exclusive purpose of maximization of middle distillate products. Being an intermediate product, middle distillate range molecules have a tendency to undergo further cracking. There is always a trade off between maximization of an intermediate range product and minimization of bottom unconverted part. This invention includes the sequence of operation and operating conditions for control of over-cracking of middle distillate in the first riser and upgradation of heavier molecules to middle distillate in the second riser. This invention provides a novel scheme for operation of two or multiple risers at entirely different operating conditions with a common regenerator. Use of so much lower temperature cracking is unusual so far. However, the applicants have found that reaction temperature has a predominant effect on the over cracking of middle distillate range products. For example, at 40 wt% 370°C- conversion, the wt% yield ratios of TCO and all other products, (i.e., dry gas, LPG, gasoline & coke) except TCO and bottom (subsequently referred as TCO/Rest ratio) are in the range of about 3.0 – 3.5 and about 1.5 – 1.8 at reaction temperatures of 425°C and 490°C respectively. The difference in the above ratio is narrowed down as the conversion increases (Figure-3).

Therefore, for maximizing TCO, low reaction temperature, low catalyst to oil ratio, as well as low catalyst activity is desirable. The applicants identified that lower catalyst/oil ratio (2 - 8) and higher WHSV of (150 - 350 hr⁻¹) along with lower riser temperature in the first riser of the process of the present invention are very important to achieve a very low degree of over cracking for producing maximum middle distillate range components. The applicants also observed that the TCO/Rest ratio is significantly affected by the 370°C- conversion level. For example, for a given catalyst and reaction temperature, if 370°C- conversion is 40%, the TCO/Rest ratio is as high as 3.2 which comes down to about 1.3 when 370°C - conversion is

increased to 70%. This shows that restricting the conversion in the first stage riser up to about 40 – 45% is very important to maximize the yield of middle distillate.

In the second riser, the operating conditions need to be different for upgradation of heavy material to lighter products. However, undue increase in severity parameters will lead to conversion of the desired middle distillate to LPG and gasoline. The applicants have discovered that operation at an intermediate severity as compared to gasoline maximization mode FCC operation is absolutely necessary. The applicants have also found that in order to reduce the yield of unconverted bottoms and improve the middle distillate selectivity, recycle to a lower elevated entry point at the bottom of the second riser is very much effective. This allows the cracking of the recycled heaviest fraction in effective contact with regenerated catalyst at relatively higher temperature and lower CRC that improves the dynamic activity of the catalyst and offers maximum cracking of the recycled feed. After cracking of the recycled part, the catalyst temperature comes down due to utilization of part of the heat for vaporization and endothermic cracking reactions of the recycled feed. Also, the coke on catalyst increases which essentially blocks some of the active sites and thereby reduces the dynamic activity of the catalyst. The contacting of catalyst having relatively lower temperature and higher coke on catalyst with the main feed, comprising the hydrocarbon fraction from the first riser having boiling points greater than or equal to about 370°C, assists to improve the selectivity of middle distillate range products out of the second riser. This contacting pattern is highly effective in increasing the overall yield of the middle distillate and reducing yield of the unwanted slurry oil.

In the present invention, the delta coke (defined as the difference in coke content of spent and regenerated catalyst) is low due to lower coke make in the extremely low severity cracking in the first riser which is expected to keep the regenerator temperature at a relatively lower level as compared to the conventional FCC operation using similar type of feedstocks. However, overall lower catalyst to oil ratio is likely to compensate for this effect and thereby maintain the regenerator temperature at least at the same level as that of conventional FCC as required for burning of coke off the catalyst.

Further details of feedstock, catalyst, products and operating conditions of the process of the present invention are described below:

Feed Stock:

Feed stock for the present invention includes hydrocarbon fractions starting from carbon no. 20 to carbon no. 80. The fraction could be straight run light and heavy vacuum gas oil, hydrocracker bottom, heavy gas oil fractions from hydrocracking, FCC, visbreaking or delayed coking. The conditions in the process of the present invention are adjusted depending on the type of the feedstock so as to maximize the yield of middle distillate. Details of the feedstock properties are outlined in the examples given hereinbelow. The above feed stock types are for illustration only and the invention is not limited in any manner to only these feed stocks.

Catalyst:

The catalyst employed in the process of the present invention predominantly comprises Y-zeolite in rare earth ultra-stabilized form. Bottom cracking components consisting of peptized alumina, acidic silica alumina or Y- alumina or a mixture thereof are also added to the catalyst formulation to produce synergistic effect towards maximum middle distillate production under the operating conditions as outlined above. It may be noted that both the first and second stage risers are charged with the same catalyst. The pore size range of the active components namely, Re-USY zeolite and bottom selective active materials are in the range of about 8 – 11 and 50 – 1000 angstroms respectively. The typical properties of the Y-zeolite based catalyst are given in Table-2.

Table – 2

Surface Area, m ² /g,	Fresh	110 – 180
	Steamed	100 – 140
% Crystallinity	Fresh	10 – 15
	Steamed	8 – 12
Unit Cell Size, °A	Fresh	24.35 – 24.75
	Steamed	24.2 – 24.6
Micro-pore area, m ² /g,	Fresh	65 – 100
	Steamed	60 – 90
Meso-pore area, m ² /g,	Fresh	45 - 80
	Steamed	40 - 50
Pore volume, cc/gm		0.25 – 0.38

In the process of the present invention, the active catalyst components are supported on relatively inactive materials such as silica/alumina or silica-alumina compounds, including kaolinites. The active components could be mixed together before spray drying or separately binded, supported and spray-dried using conventional spray drying technique. The spray-dried micro-spheres are washed, rare earth exchanged and flash dried to produce finished catalyst particles. The finished micro-spheres containing active materials in separate particles are physically blended in the desired composition. The preferred range of physical properties of the finished fresh catalyst as required for the process of the present invention:

Particle size range, micron : 20-120
Particle below 40 microns, wt% : < 20
Average particle size, micron : 50-80
Average bulk density, micron : 0.6 – 1.0

Typically, the above properties and other related physical properties, e.g., attrition resistance, fluidizability etc. are in the same range as used in the conventional FCC process.

Products:

The main products in the process of the present invention is the middle distillate components namely, heavy cracked naphtha (HCN : 150 – 216°C) and light cycle oil (LCO : 216 – 370°C). The sum total of these two fractions, which is referred to as total cycle oil (TCO : 150 – 370°C) is obtained with a yield up to about 50 - 65 wt% of the feed. The other useful products of the process of this invention are LPG (5 - 12%) and gasoline (15 - 25 wt%). A range of other product yields from first and second stage risers are summarized in the following Table - 3:

Table – 3

	Yield, wt% of feed		
	From first reactor	From second reactor	Combined yield from both first & second
Dry Gas (C ₁ + C ₂)	0.1 – 0.35	1-1.5	0.5 – 1.5
LPG (C ₃ + C ₄)	3 – 4	8 – 12	5 – 12
Gasoline (C ₅ – 150°C)	10 – 15	25 – 30	15 – 30
Heavy Naphtha, (150–216°C)	8 – 10	10 – 13	10 – 15
Light Cycle Oil, (216–370°C)	35 – 45	25 – 35	40 – 50
Total Cycle Oil (150–370°C)	45 – 50	30 – 40	50 – 65
Bottom (370°C+)	40 – 60	10 – 20	5 – 15
Coke	1 – 3	2 – 5	2 – 4

The invention and its embodiments are described in further detail hereunder, with reference to the following examples, which should not be construed to limit the scope of the invention in any manner. Various modifications of the invention that may be apparent to those skilled in the art are deemed to be included within the scope of the present invention.

Example-1 (PRIOR ART)

Yield of middle distillate at different conversions in conventional FCC operation

This example illustrates the change in yield of the middle distillate product (TCO) at different conversion levels under conventional FCC conditions. -216°C conversion is defined as the total quantity of products boiling below 216°C including Coke. Similarly -370°C conversion is defined as the total quantity of products boiling below 370°C including Coke. The experiments were conducted in standard fixed bed Micro Activity Test (MAT) reactor described as per ASTM D-3907 with minor modifications indicated subsequently as modified MAT. The catalyst to be used is first steamed at 788°C for 3 hours in presence of 100% steam. The physico-chemical properties of the feed used in the modified MAT reactor are given in the following Table – 4 & 5.

Table – 4

Density @ 15°C, gm/cc	0.8953
CCR, wt%	0.32
Sulfur, wt%	1.12
Basic Nitrogen, PPM	366
Paraffins, wt%	44.4
Naphthenes, wt%	18.1
Aromatics, wt%	37.6
Nickel, PPM	< 1
Vanadium, PPM	< 1

The runs were taken at a reaction temperature of 495°C, feed injection time of 30 seconds with WHSV in the range of 40 – 120 hr⁻¹. Catalysts used in this example are catalyst A & B which are commercially available FCC catalyst samples having properties as shown in the Table-6.

Table – 5

ASTM Distillation (D1160) :	
Volume %	Temperature, °C
IBP	299
5 / 12 / 15 / 20 / 30 / 40	342 / 358 / 371 / 381 / 401 / 418
50 / 60 / 70 / 80 / 90 / 95	432 / 444 / 458 / 474 / 497 / 515
FBP	550

Table – 6

		Catalyst – A	Catalyst – B
Surface Area, m ² /gm	Fresh	170	272
	Steamed	103	208
Pore Volume, cc/gm		0.22	0.26
ABD, gm/cc		0.81	0.79
Crystallinity, %	Fresh	18.9	27.7
	Steamed	-	23.2
UCS, °A	Fresh	24.61	24.56
	Steamed	24.32	24.31
Chemical Analysis, wt%			
Al ₂ O ₃		56.5	30.85
Re ₂ O ₃		1.44	1.03
Fe		0.49	0.53
APS, microns		74	77

The product yields along with conversions are given in Table-7 wherein it is observed that as both -216°C and -370°C conversions increase, TCO yield increases up to an optimum value and thereafter, it reduces with further increase in conversion. TCO being an intermediate product, undergoes further cracking as reaction severity increases. Therefore, in order to maximize TCO yield, the over-cracking is to be restricted.

Table – 7

Product Yield, wt%	Catalyst A			Catalyst B			
W/F, Min.	0.51	0.62	0.94	0.44	0.51	0.63	0.94
Hydrogen	0.018	0.021	0.041	0.025	0.025	0.033	0.046
Dry gas	0.44	0.56	1.14	0.59	0.64	0.86	1.46
LPG	7.33	8.82	13.61	6.18	6.97	10.09	12.34
Gasoline	19.32	23.43	30.78	17.20	20.50	25.03	30.94
TCO	40.09	41.53	37.79	36.33	37.97	39.94	37.67
Bottom (370°C+)	31.81	24.52	14.25	38.73	32.82	22.80	14.92
Coke	0.99	1.13	2.39	0.95	1.08	1.25	2.61
-216°C Conversion	40.17	47.50	62.45	34.96	40.34	49.98	60.99
-370°C Conversion	68.19	75.48	85.75	61.27	67.18	77.20	85.08

Example-2

Effect of reaction temperature on middle distillate yields at same conversion

This example illustrates the effect of reaction temperature on the yield of middle distillate at a given -216°C conversion. The experiments were conducted in the modified MAT reactor with the same feed as mentioned in Example-1, at two different temperatures, viz., 425°C and 495°C. Catalyst employed here is catalyst C which is commercially available FCC catalyst of following properties as shown in the Table – 8.

Table – 8

		Catalyst – C
Surface Area, m ² /gm	Fresh	172
	Steamed	119
Pore volume, cc/gm		0.32
Crystallinity, %	Fresh	13.80
	Steamed	10.20
UCS ⁰ A	Fresh	24.55
	Steamed	24.31
Chemical Analysis, wt%		
RE ₂ O ₃		0.69
Al ₂ O ₃		36.40
Na ₂ O		0.11
Particle size, micron / wt%		
-20 / -40 / -60 / -80 / -105 / -120		3 / 16 / 32 / 56 / 77 / 86
APS, micron		76

Table – 9

Temperature, °C Π	425		495	
-216°C conversion, wt%	30	50	30	50
W/F, Min.	1.1	2.7	0.10	0.5
<u>Yield Pattern, wt%</u>				
Dry gas	0.20	0.42	0.38	0.56
LPG	4.10	9.1	5.07	10.72
Gasoline	14.94	23.52	16.00	24.58
Heavy naphtha	9.50	14.27	7.11	11.20
LCO	28.68	32.00	25.80	24.50
TCO	38.18	46.27	32.91	35.70
Bottom (370°C+)	41.32	18.00	44.20	25.40

Coke	1.26	2.69	1.44	2.94
370 °C Conversion	58.68	82.00	55.80	74.60
TCO /Rest	1.86	1.29	1.43	0.92

The conversion was varied by changing W/F ratio. The product yields are compared at the same -216°C conversion but at different temperatures. It is noted from Table-9 that at higher temperature, TCO yield and more importantly the TCO/Rest ratio (the ratio of TCO yield and yield of other products e.g., dry gas, LPG, gasoline and coke except bottom and TCO) are much lower in the case of higher reaction temperature. For example, at a given -216°C conversion, TCO yield at 425°C temperature is about 6 - 10% higher than that at 495°C. The other significant point is that at a low temperature of 425°C, it has been possible to get 46% TCO yield (per pass) at 50% -216°C conversion. Similarly, there is a significant improvement in TCO/Rest ratio for 425°C as compared to that of 495°C at same conversion. This clearly demonstrates that in order to conserve middle distillate range molecules, low reaction temperature is a desirable parameter.

Example-3

First stage riser cracking conditions

This example illustrates the significance of first stage riser cracking conditions, e.g., temperature, catalyst/oil ratio and conversion, on the yield of middle distillate and other products while employing commercially available FCC catalysts A and C, properties of which are described in Example-1 & 2 respectively. The tests were conducted in modified fixed bed MAT unit with same feed as described in Example-1. Yield data were generated at different conversion level for the catalysts as indicated above and the yields of different products were obtained. TCO/Rest ratios at different conversion levels are plotted in Figure-3, from which it is observed that for both the catalysts, the TCO/Rest ratio increases as the -370°C conversion is reduced. Therefore, it is important to note that the per pass -370 °C conversion in the first stage riser should be kept below about 45% and preferably below 40%.

From Figure-3, it is also observed that the TCO/Rest ratio is a strong function of the reactor temperature for a given conversion and catalyst. For example, with catalyst C, while

reducing reaction temperature from 490 to 425°C, the TCO/Rest ratio is increased from 3.4 to 3.75 at about -370°C conversion level of 40%. This clearly shows that for the first stage cracking, the reaction temperature should be kept lower, preferably in the range of about 425 – 450°C.

Example - 4

Catalyst characteristics for middle distillate maximization

One of the important observations as illustrated in Example-3, is that for maximization of middle distillate yield, it is desirable to restrict the per-pass conversion to within about 40 – 45%, and to operate the first stage riser at lower reaction temperature. In this example, we illustrate the importance of catalyst characteristics to obtain higher yield of middle distillate out of the dual/ multi – stage risers.

MAT activity is measured in ASTM MAT units using a standard feedstock and defined as the wt% of products boiling below 216°C including coke at ASTM conditions. All other experiments were conducted at a temperature of 425°C in the modified MAT reactor with the same feed as described in Example-1 and different catalysts. The important properties of the catalysts and the yield / conversion data are compared in Table-10.

Table-10

	Catalyst – A	Catalyst-C	Catalyst-D	Catalyst-E
Surface Area, m ² /gm	103	119	110	20
Zeolite Area, m ² /gm	59	80	62	-
Rare earth content, wt%	1.44	0.69	1.40	-
Matrix Area, m ² /gm	44	39	48	-
Zeolite / Matrix ratio	1.34	2.05	1.29	-
MAT Activity	71.38	74.02	70.19	13.55
TCO Yield at 40% -370°C Conversion	31.00	32.01	30.90	31.20

TCO yield/Rest ratio at 40% -370°C conversion	3.44	4.00	3.39	3.30
W/F for 40% -370°C conversion	0.22	0.25	0.22	3.5

Table -11

	Catalyst-A	Catalyst-C	Catalyst-D
TCO Yield at 80% -370°C Conversion	38.45	34.78	43.0
TCO yield/Rest ratio at 80% -370°C conversion	0.95	0.80	1.08

It is seen that the zeolite/matrix ratio, TCO yields at 40% -370°C conversion, TCO / Rest ratio are in the order of C > A > D. In catalyst C, the available active matrix is adequate to crack the large molecules which are crackable under the prevailing operating conditions but it requires slightly higher W/F ratio. Higher zeolite quantity (proportion) is also synergistically taking part in the over all cracking activity but the conversion of middle distillate to lighter products is not increasing corresponding to higher zeolite content due to lower temperature. However for catalyst-E, whose activity is extremely low, at 40% of -370°C conversion, both TCO yield and TCO/Rest ratio is comparable to those with the higher active catalysts. But W/F ratio required to achieve 40% -370°C conversion is much higher which is difficult to achieve. At comparable W/F ratio, -370°C conversion will be very low, producing very low amount of TCO. Therefore, such low active catalyst is not useful for producing maximum distillate.

Experiments with catalysts A, C & D at a reaction temperature of 495°C corresponding to the second riser conditions were taken and the TCO yield and TCO/ Rest ratio are compared at -370°C conversion of 80% in Table-11. Both the TCO yield and TCO/ Rest ratio are found to be in the order of D > A > C. It may be noted that the zeolite / matrix ratio is just in the reverse order i.e., C > A > D. The higher quantity of zeolite as well as the high zeolite/matrix ratio in catalyst C, is resulting in overcracking of middle distillate range molecules into lighter products. For a given -370°C conversion, the -216°C conversion is much higher for catalyst C. It is quite clear that the catalyst which is supposed to be the best in the first riser conditions, may not be that much good for the second riser conditions as for as TCO maximization is concerned. This

demonstrates that in order to achieve maximum TCO and minimum Bottom yield, some optimization of the catalyst properties is essential.

Example – 5

Impact of cracking conditions for second stage riser operation

This example illustrates the significance of second stage riser cracking conditions e.g., temperature, catalyst/oil ratio and conversion on the yield of middle distillate. The tests were conducted in modified fixed bed MAT unit as described in Example-1, using catalyst C, at the temperature of 425, 490 and 510°C. The feed stock used is 370°C⁺ product obtained from first stage cracking in circulating riser FCC pilot plant, the properties of which is summarized in Table-13. Product yields data were generated at different conversion levels at different temperatures for catalyst C and according the TCO/Rest ratios at different conversion levels are plotted in Figure-4.

Table – 12

Density, gm/cc @ 15°C	0.903
CCR, wt%	0.43
Sulfur, wt%	1.75
Olefins, wt%	Nil
Saturates, wt%	59.0
Aromatics, wt%	41.0

From the Figure-4, it is observed that at a given temperature, the TCO/Rest ratio increases as the -370°C conversion reduces. Also, at a given -370°C conversion, TCO/Rest ratio improves as the reaction temperature reduces. For example, at about -370°C conversion of about 55%, TCO/Rest ratio increases from 1.22 to 1.34 as the temperature is reduced from 510 to 490°C. This clearly shows that even for the second stage cracking, the reaction temperature should be kept preferably lower. However, it will also lead to generation of higher quantity of bottom at same W/F ratio. At 425°C, W/F required to crack the 370°C⁺ product from first stage cracking along with the recycle stream (unconverted part from the second riser) will be very high

and hence difficult to achieve. Another important fact is that the mean average boiling point (MeABP) of second riser combined feed is definitely higher than that of first riser. Operation at lower temperature than the MeABP of the second riser combined feed is not desirable as it will lead to non-selective thermal cracking of the non-vaporized feed producing higher quantity of Coke and Dry gas. Considering these, it has been established that in the second riser, the reaction temperature should be preferably kept in the range of 460 - 510°C.

Example – 6

Combined effect of two stage cracking on middle distillate yield

In this example, the yields from two stage catalytic cracking for maximization of middle distillate is demonstrated. The experiments have been conducted using catalyst C in continuously circulating fluid bed pilot plant of feed rate 0.75 kg/hr where both the riser and regenerator are operated isothermally. The feed is the same as mentioned in Example-1. After first stage cracking at 425°C, the product is separated into 370°C– and 370°C+ fractions. In the second stage, the 370°C+ fraction is cracked at 495°C using the same catalyst as used in the first stage. The product yields from the first and second stage cracking and also the combined yields are given in Table-13.

Table-13

	first stage	second stage	Combined yields
Temperature, °C	425	495	
<u>Yield Pattern, wt%</u>			
Dry gas	0.26	1.28	0.81
LPG	3.37	16.65	10.55
Gasoline	10.65	26.03	21.88
Heavy naphtha	8.54	13.31	14.28
LCO	32.33	19.47	40.73
TCO	40.87	32.78	55.01
370 °C +	43.25	20.44	8.82
Coke	1.70	2.85	2.93

It is clearly seen that the ratio of yield of TCO and the sum of yields of dry gas, LPG, gasoline and coke (TCO/Rest) is very high in case of the first stage cracking, which is essentially contributing higher TCO yield for the overall process. For second stage cracking, the TCO/Rest ratio is similar to that of conventional distillate mode FCC unit as the severity required for minimizing the bottom yield is high enough to crack significant portion of TCO produced from heavy molecule cracking.

The yield comparison between single and dual riser cracking at similar -216°C conversion with same catalyst and feed is compared in Table-14. It is seen that for same -216°C conversion, -370°C conversion is much higher resulting about 20% higher yield of TCO in case of two stage cracking. This establishes the workability of the concept of the present invention where process schemes, catalyst and operating conditions are such that TCO over-cracking is restricted with simultaneous upgradation of heavy molecules to TCO range molecules. Here, the first riser operates to extract as much TCO as possible while minimizing the yields of lighter products and the second riser is operated to upgrade as much bottom as possible while maximizing the yield of TCO. This process overcomes the trade off between lower bottom yield and higher TCO yield.

Table-14

	Dual riser	Single riser
Temperature, $^{\circ}\text{C}$	425 & 495	495
Yield Pattern, wt%		
Dry gas	0.81	0.56
LPG	10.55	10.72
Gasoline	21.88	24.58
Heavy naphtha	14.28	11.20
LCO	40.73	24.50
TCO	55.01	35.70
370°C^{+}	8.82	25.40

Coke	2.93	2.94
-216 conversion, wt%	50.45	50.0

Example – 7**Comparison of Micro-reactor & Circulating pilot plant data**

This example shows the comparison of individual product yields obtained from Micro-reactor and circulating Pilot Plant using the same catalyst and feedstock at a similar -216°C conversion range. From the data summarized in Table-16, it is noticed that at similar conversion, there is an excellent match in gasoline, TCO and bottom yields. The main difference is coming in the yields of dry gas, LPG and coke. This is mainly due to the non-selective thermal cracking reactions occurring at the riser bottom as well as at the end of the riser in the pilot plant. This has resulted in relatively higher yield of dry gas and coke in the pilot plant riser. This example demonstrates that so far as the yields of TCO and un-reacted bottom are concerned, the inferences drawn based on either Micro-reactor or Pilot Plant data are going to be same.

Table-15

	Pilot Plant data		Micro-reactor data	
Feed rate, gm/min	12.9	13.3	-	-
CCR, gm/min	55.5	53.0	-	-
Cat/Oil (w/w)	4.29	3.98	-	-
W/F, min.	-	-	0.609	0.501
Contact time, sec	-	-	30	30
-216 Conversion, wt%	29.86	25.0	29.39	24.93
<u>Product Yields, wt%</u>				
Dry gas	0.62	0.36	0.17	0.13
LPG	8.28	6.29	9.96	8.61
Gasoline	11.82	10.7	12.00	10.65
Heavy Naphtha	7.15	5.92	5.80	4.62
LCO	27.3	26	28.29	26.61
TCO	34.45	31.9	34.09	31.23
370°C +	42.82	49	42.31	48.46
Coke	2.00	1.71	1.46	0.91

Example – 8

Comparison of the yields of present two stage process in present invention, commercial FCCU and two stage hydrocracker

The product yields of the present invention are compared with that of commercial distillate mode FCC and two-stage hydrocracker units in Table-17. The data for the process of the present invention is the combined yield obtained from two stage cracking where the two risers are operated at 425°C and 495°C, respectively.

Table – 16

Product yields, wt% of feed	Distillate mode FCC	Present process	Yields, wt% of feed	Distillate mode Hydrocracker	Present process
Dry gas	2.50	0.78	Dry gas	1.74	0.70
LPG	10.5	10.55	LPG	2.91	9.11
Gasoline (C ₅ -150°C)	27.5	21.88	Gasoline (C ₅ -120°C)	16.28	12.86
Heavy Naphtha a (150-216°C)	12.5	14.28	(120-216°C) (120-285°C)	- 27.91	18.41 -
LCO (216-370°C)	30.0	40.73	(216-390°C)	-	50.39 -
TCO (150-370°C)	42.5	55.01	(120-390°C)	73.26	68.80
370°C ⁺	12.75	8.82	390°C ⁺	5.81	5.85
Coke	4.25	2.93	Coke	-	2.68
-216°C conv.	57.25	50.45	-216°C conv.	-	-
-370°C conv.	87.25	91.18	-390°C conv.	94.19	94.15

It is observed that in the process of the present invention, the TCO yield is higher by about 12.50% as compared to the yield from a commercial FCC unit. By varying the cut point of TCO from 150 - 370°C to 120 - 390°C as reported for the hydrocracker unit, and processing the hydrocarbon product fraction from the first riser having boiling points greater than or equal to 390°C in the second riser, the yield of TCO increases by about 14 wt%, which is only about 5% less than that from the commercial hydrocracker unit. Also, the conversion of hydrocarbon products having boiling points less than or equal to 390°C (-390°C conversion) is similar to what is achievable in a hydrocracker and -370°C conversion is better than the distillate mode FCC unit. This demonstrates that, without using external hydrogen and operating under very high pressure, it is possible to produce higher yields of middle distillate product which are close to that from a distillate mode two stage hydrocracker unit.

Example -9

Comparison of properties of TCO obtained in the process of the present invention with middle distillate products obtained from commercial FCCU and two stage Hydrocracker

The properties of the TCO obtained from the process of the present invention is compared with TCO from commercial distillate mode FCC and Diesel from distillate mode two stage Hydrocracker units which is given in Table-17.

Table -17

	Process of the present invention		Distillate mode FCC	Distillate mode Hydrocracker
	1	2	3	4
	TCO	Middle distillate	TCO	Diesel
TBP cut point, °C	150 - 370	120 - 390	150 - 370	150 - 390
Density @ 15°C, gm/cc	0.8793	0.8863	0.8654	0.835
Pour point, °C	0.7	36	0 - 2	6 - 10
Kinematic Viscosity @ 50°C, CST	2.20	7.00	2.7	9.0

PONA Analysis, wt%				
Olefins	19.97	6.82	18.6	Nil
Saturates	24.64	49.26	22.1	91
Aromatics	55.39	43.92	59.3	9
Cetane no.	36.22	38.39	28 - 30	63

Expectedly, the quality of diesel range product obtained from a hydrocracker is much superior in terms of cetane No., olefin and aromatics contents etc. than the cracked products made without using hydrogen. Mainly, the high aromatics content in cracked middle distillate product contribute to poor cetane quality. However, the viscosity and the pour point of hydrocracker diesel is poor as compared to TCO from a conventional FCC unit or the process of the present invention. From column 1 & 3, it is seen that the cetane No. of TCO obtained from the present process is higher by 6 units than TCO from conventional distillate mode FCCU. All other properties including the pour point are almost in the same range. In column 2, the properties of the product fraction of 120–390°C range for the present process are listed. While cetane number of this fraction is still higher, the pour point, as well as the viscosity, are also higher. This has been mainly contributed by the hydrocarbon fraction of 370 – 390°C cut from the first riser product of the present process. The pour point as well as the viscosity of this product fraction is very high and hence its inclusion in the middle distillate product is not desirable. If we take the 120 – 370°C cut from the first riser product and the 120 – 390°C cut from the second riser (while processing the 370°C+ part of the first riser product into the second riser), the pour point and the kinematic viscosity @ 50°C become 0.95°C and 2.44 CST respectively, which are almost same as that of 150 – 370°C product of the present invention as shown in the column 1 of Table- 18. Additionally, by this approach, the yield of the middle distillate increases from about 55 wt% to 63.6 wt% without any adverse impact on flash point.

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A MULTI STAGE SELECTIVE CATALYTIC CRACKING PROCESS AND A SYSTEM FOR PRODUCING HIGH YIELD OF MIDDLE DISTILLATE PRODUCTS FROM HEAVY HYDROCARBON FEEDSTOCKS

Field

This invention relates to a process and a system for the production of middle distillate products comprising hydrocarbons having carbon atoms in the range of C_8 to C_{24} in high yield, from heavier petroleum fractions through multistage catalytic cracking of varying severity levels with solid acidic catalyst without using external hydrogen.

Background

Conventionally, middle distillate range products e.g. Heavy Naphtha, Kerosene, Jet fuel, Diesel oil and Light Cycle Oil (LCO) are produced in petroleum refineries by atmospheric/vacuum distillation of petroleum crude and also by the secondary processing of vacuum gas oil and residues or mixtures thereof. Most commonly practiced commercial secondary processes are Fluid Catalytic Cracking (FCC) and Hydrocracking. Hydrocracking employs porous acidic catalysts similar to those used in catalytic cracking but associated with hydrogenation components such as metals of Groups VI and VII of the Periodic Table to produce good quality of middle distillate products in the boiling range of C_8 - C_{24} hydrocarbons. An excess of hydrogen is supplied to the hydrocracking reactor under very high pressure (150-200 atm.) and at a relatively lower temperature (375-425°C) in fixed bed reactors with two phase flow. Due to severe hydrogenation, all hydrocarbon products from Hydrocracker are highly saturated with low sulfur and aromaticity. The yield of middle distillate hydrocarbons (126-391°C boiling range) in hydrocracking is typically very high up to 65 - 80 wt% of feed.

FCC process, on the other hand, is employed for essentially producing high octane Gasoline and LPG. In countries, where demand of middle distillate product is higher, Heavy Cracked Naphtha (HCN: $C_8 - C_{12}$ hydrocarbons) and Light Cycle Oil (LCO: $C_{13} - C_{24}$ hydrocarbons) production are maximized by manipulating operating variables so as to vary the reaction and regenerator severity levels. U.S. Patent Nos. 3,894,931 and 3,894,933 address such operations. Typically, diesel yield in FCC is maximized by maintaining a lower reaction and regeneration severity (i.e., lower regenerator and reactor top temperature) and recycling of unconverted residual products. Catalyst with lower zeolite/matrix ratio and MAT (Micro Activity Test) activity of 60-70 is normally preferred. By proper selection of FCC variables and innovations involving catalyst type and recycle of Heavy Cycle Oil and residual Slurry oil, distillate yield can be increased by considerable amount at the expense of Gasoline yield. As the FCC unit operation is shifted from gasoline mode to middle distillate maximization mode, the LCO cetane number increases and thus could be more useful for blending to diesel pool.

However, while running at low severity operations, for maximizing diesel yield, the unconverted bottom yield also increases to a significant extent and sometimes may even exceed 20 wt% of fresh feed as against 5-6 wt% for usual gasoline mode operation. The other drawback of low severity operation is the high amount of recycle oil being used in the riser bottom with fresh feed for further cracking. Firstly, this reduces the throughput of riser reactor and secondly, with single riser and product fractionator, the recycle is nonselective. This results into recycling of un-crackable, aromatic components into the riser and thereby increases Coke and Gas without appreciably increasing the conversion level. Consequently, Diesel yield from FCC with the conventional cracking catalyst could be maximized upto 40-45 wt% in spite of running at low

reaction severity (495°C riser temperature) and fairly higher recycle ratio (30% of fresh feed).

Besides the operation of conventional FCC in middle distillate maximization mode, there are several other processes aiming for improvement in middle distillate yield. U.S. Pat. No. 5,098,554 discloses a process of fluid catalytic cracking with multiple feed injection points where fresh feed is charged to upper injection points and unconverted slurry oil is recycled to a location below the fresh feed nozzles. Essentially, the process conditions are similar to that of gasoline mode FCC operation (e.g., 527°C riser top temperature) which favors gasoline production. By adopting split feed injection, middle distillate yield is marginally increased at the expense of Gasoline yield.

U.S. Pat. No. 4,481,104 describes about an ultra-stable Y-zeolite of high framework silica to alumina ratio having low acidity, large pores, use of which in catalytic cracking of gas oil, enhances distillate yield with production of low Coke and Dry gas. It may be noted that yield of 420 – 650°F fraction is maximize about 28 wt% of feed and as 650°F- conversion increases beyond 67 wt%, the yield of 420–650°F fraction further reduces. Therefore, as discussed earlier, yield of the distillate is relatively more only at the higher yield of unconverted fraction.

Yet another process in U.S. Pat. No. 4,606,810 discloses a scheme of two riser cracking for improving total gasoline plus distillate yield. Here, the feed is first cracked in the first riser with spent catalyst from the second riser and the unconverted part is further cracked in a second riser in presence of regenerated catalyst. The basic operation is of high severity producing maximum amount of Gasoline and the yield of LFO is around 15 – 20 wt% of feed. It may also be

noted that while increase in Gasoline yield is in the range of 7.5 – 8.0 wt%, increase in LFO yield is merely in the range of 1.5 – 3.0 wt% on fresh feed basis.

Two stage processing of hydrocarbon feedstock has been employed by different researchers in the field of catalytic cracking. Several processes have been developed in which first stage processing removes metals and Conradson carbon residue (CCR) impurities from feed using a low activity cheap contact material with abundant surface area. The demetallized feed is then processed in a more conventional second stage reactor under high severity to maximize the conversion and gasoline production. U.S. Pat. No. 4,436,613 describes such a process of two stage catalytic cracking using two different types of catalyst. In the first stage, the CCR materials and metals are separated from the rest of the feedstock along with mild cracking over a relatively lower active catalyst. The residual un-cracked product of the first stage is then contacted with a high active catalyst under higher reaction severity for gasoline maximization. It may be noted that in this process, two dedicated strippers and regenerators are used to avoid the mixing of two different types of catalysts.

Dual riser high severity catalytic cracking process described in U.S. Pat. No. 3,928,172 utilizes a mixture of large pore REY zeolite catalyst and a shape selective zeolite catalyst where gas oil is cracked in the first riser in the presence of the aforesaid catalyst mixture. The Heavy Naphtha product from the first riser and/or virgin straight run Naphtha are cracked in the second riser in the presence of catalyst mixture to produce high octane Gasoline together with C₃ and C₄ olefins. U.S Pat. No. 4,830,728 discloses a process for upgrading straight run Naphtha, catalytically cracked Naphtha and mixtures thereof in a multiple fluid catalytic cracking operation utilizing mixture of amorphous cracking catalyst and/or large pore Y-zeolite based catalyst and shape selective ZSM-5 to produce high octane gasoline.

U.S. Pat. No. 5,401,387 describes a process of multistage catalytic cracking where the first stage cracks a first feed over a shape selective zeolite to produce lighter products rich in iso-compounds which may be used for making ethers. A second feed which may include 700°F+ liquid from first stage is cracked in the second stage. Another process as described in U.S. Pat. No. 5,824,208, discloses a scheme in which hydrocarbon is initially contacted with cracking catalyst forming a first cracked product which after recovering of the product having boiling point of more than 430°F, is subjected to cracking in a second riser. The basic objective of this invention is to maximize the yield of light olefins and minimize the formation of aromatic compounds by avoiding undesirable hydrogen transfer reactions.

So far, most of the prior art methods have concentrated on multiple riser catalytic cracking for maximization of gasoline yield and its octane numbers, increased yield of iso-olefin for production of ethers, increased yield of light olefins, etc. From the prior art information and also from our experience of operating low severity FCC units, it is quite clear that maximizing middle distillate yield in FCC (without using external hydrogen) is not achieved beyond a level of 40-45 wt% of fresh feed. Further, persons involved in fluid cracking would be aware that middle distillate being an intermediate product in the complex catalytic cracking reactions, its maximization is very difficult because when the severity is increased, it is re-cracked to lighter hydrocarbons.

Objects

Accordingly, the main object of the present invention aims to propose a novel catalytic cracking process for producing middle distillate products in very high yield (about 50-65 wt%).

Another object is to provide a multiple riser system that enables the production of middle distillate products including Heavy Naphtha and Light Cycle Oil in high yield.

Yet another object of the invention is to provide a multiple riser system to produce higher yield of Heavy Naphtha and Light Cycle Oil as compared to the prior art processes employing catalytic cracking of petroleum feedstock without any use of external supply of hydrogen.

A further objective of the process is to minimize the yield of unwanted dry gas and coke and also the yield of unconverted bottom products, at the same time, improving the cetane quality of the middle distillate product.

Summary

According to the present invention, there is provided a novel process for catalytic cracking of various petroleum based heavy feed stocks in the presence of solid zeolite catalyst and high pore size acidic components for selective bottom cracking and mixtures thereof, in a multiple riser type system wherein continuously circulating fluidized bed reactors are operated at different severities to produce middle distillate products in high yield, in the range of 50-65 wt% of fresh feed.

The invention also provides an improved system for catalytic cracking of heavy feed stock to obtain middle distillate products in high yield, employing the process herein described.

Detailed Description

The invention relates to a multi stage selective catalytic cracking process for producing high yield of middle distillate products having carbon atoms in the

range of about C_8 to C_{24} , from heavy hydrocarbon feedstock, in the absence of added hydrogen, said process comprising the steps of:

- i) contacting preheated feed with a mixed catalyst in a first riser reactor under catalytic cracking conditions including catalyst to oil ratio of 2 to 8, WHSV of $150-350 \text{ hr}^{-1}$, contact period of about 1 to 8 seconds and temperature in the range of about 400°C to 500°C to obtain first cracked hydrocarbon products;
- ii) separating the first cracked hydrocarbon products from the first riser reactor into a first fraction comprising hydrocarbons with boiling points less than or equal to 370°C and a second fraction comprising unconverted hydrocarbons with boiling points greater than or equal to 370°C ;
- iii) cracking the unconverted second fraction from the first riser reactor comprising hydrocarbons having boiling points greater than or equal to 370°C , in the presence of regenerated catalyst, in a second riser reactor operating under catalytic cracking conditions including WHSV of $75-275 \text{ hr}^{-1}$, catalyst to oil ratio of 4-12 and riser top temperature of $425 - 525^\circ\text{C}$ to obtain second cracked hydrocarbon products;
- iv) separating the catalytically cracked products from the second riser reactor alongwith cracked products comprising hydrocarbons having boiling points less than equal to 370°C , from the first riser reactor in a main fractionating column to yield cracked products comprising dry gas, LPG, gasoline, middle distillates, heavy cycle oil and slurry oil;
- v) recycling the entire heavy cycle oil comprising hydrocarbons having boiling points in the range of 370°C to 450°C and full or part of the slurry oil having boiling points greater than or equal to

450°C, into the second riser reactor at a vertically displaced position lower than the position of introduction of the main feed comprising bottom unconverted hydrocarbon fraction having boiling points greater than or equal to 370°C from the first riser reactor to obtain middle distillate products comprising hydrocarbons having carbon atoms in the range of $C_8 - C_{24}$ ranging from about 50 to 65 wt % of the feed stock.

- iv) Optionally, recycling the fraction of unconverted hydrocarbons with boiling points greater than or equal to 370°C, obtained in step (v) in riser reactors by repeating steps (iii) to (iv) to obtain substantially pure middle distillate products.

In an embodiment, the feed stock is selected from petroleum based heavy feed stock, such as vacuum gas oil (VGO), visbreaker / coker heavy gas oil, coker fuel oil, hydrocracker bottom, etc.

In another embodiment, mixed catalyst is obtained from an intermediate vessel used for mixing the spent catalyst from the common stripper or preferably first stripper with the regenerated catalyst from the common regenerator and charging the mixed catalyst with coke content in the range of about 0.2 to 0.8 wt% to the bottom of the first riser at a temperature of 450 - 575°C.

In another embodiment, the exit hydrocarbon vapors from the first and second risers are quickly separated from respective spent catalysts using respective cyclones and/or other conventional separating devices to minimize the overcracking of middle distillate range products into undesirable lighter hydrocarbons.

In yet another embodiment, the spent catalysts from the first and second riser reactors are passed through respective dedicated catalyst strippers or a common stripper to render the catalysts substantially free of entrained hydrocarbons.

In a further embodiment, the regenerated catalyst with coke content of less than 0.4 wt% is obtained by burning a portion of the spent catalyst from the first stripper, the spent catalyst from the second stripper or the common stripper in a turbulent or fast fluidized bed regenerator in the presence of air or oxygen containing gases at a temperature ranging from 600°C to 750°C.

In another embodiment, the catalyst between the fluidized bed riser reactors, strippers and the common regenerator is continuously circulated through standpipe and slide valves.

In yet another embodiment, the critical catalytic cracking conditions in the first reactor including mixed regenerated catalyst result in very high selectivity of middle distillate range products and conversion of hydrocarbon products of boiling point less than or equal to 370°C at lower than 50 wt% of the fresh feed.

In another embodiment, the catalyst comprises of a mixture of commercial ReUSY zeolite based catalyst having fresh surface area of 110-180 m²/gm., pore volume of 0.25-0.38 cc/gm and average particle size of 60-70 micron along with selective acidic bottom upgrading components in the range of 0-10 wt%.

In still another embodiment, the unconverted heavy hydrocarbon fraction from second riser recycled into the second riser ranges from about 0-50 wt% of the main feed rate to the second riser, depending on the nature of the feedstock and operating conditions kept in the risers.

In yet another embodiment, amount of steam for feed dispersion and atomization in the first and the second riser reactors is in the range of 1-20 wt% of the respective total hydrocarbon feed depending on the quality of the feedstock.

In further embodiment, the spent catalyst resides in the stripper for a period of upto 30 seconds.

In another embodiment, pressure in the first and second riser reactors are in the range of 1.0 to 4.0 kg/cm²(g).

In yet another embodiment, the regenerated catalyst entering at the bottom of the second riser reactor has coke of about 0.1-0.3 wt% at a temperature of about 600-750°C and is lifted by catalytically inert gases.

In a further embodiment, the combined Total Cycle Oil (150-370°C) product which is a mixture of Heavy naphtha (150-216°C) and Light cycle oil (216-370°C), has higher cetane number than that from conventional distillate mode FCC unit and other properties such as specific gravity, viscosity, pour point, etc. are in the same range as that of commercial distillate mode FCC unit.

In still another embodiment, changing the cut point of the TCO from the first riser to 120-370°C, processing 370°C+ part of the first riser product in the second riser, and changing the cut point of TCO from second riser to 120-390°C, the yield overall combined TCO product increases by 8-10 wt% and the combined TCO product has same properties but improved cetane number as that of TCO from commercial distillate mode FCC unit.

Brief description of the accompanying drawings:

The invention is illustrated hereinbelow with reference to the following accompanying drawings, wherein :

Fig.1 shows conventional fluid catalytic cracking single riser system.

Fig.2 shows a fluidized catalytic cracking two riser system of the present invention.

Fig.3 is a graph showing the ratio of TCO Yield / Yields of (Dry gas+LPG+Gasoline+ Coke) Vs. -370°C conversion with first riser feed at two different temperatures (425°C & 490°C).

Fig.4 is a graph showing the ratio of TCO Yield / Yields of (Dry gas+LPG+ Gasoline+Coke) Vs. -370°C conversion with second riser feed at two different temperatures (490°C & 510°C).

Description of Fig.1 :

In the conventional Fluid Catalytic Cracking (FCC) unit, fresh feed (1) is injected at the bottom of the riser (2) which comes into contact with the hot regenerated catalyst from the regenerator (3). The catalyst along with hydrocarbon product vapors ascends the riser and at the end of the riser spent catalyst is separated from the hydrocarbon vapor and subjected to steam stripping. The hydrocarbon vapors from the riser reactor is sent to a main fractionator column (4) for separating into the desired products. The stripped catalyst is passed to the regenerator (3) where the coke deposited on the catalyst is burnt and the clean catalyst is circulated back to the bottom of the riser.

The fluidized catalytic cracking two riser system of the invention is schematically shown in Fig.2. and described in detail hereinbelow.

The fluidized bed catalytic cracking system for the production of high yield of middle distillate products comprising hydrocarbons having carbon atoms in the range of C_8 to C_{24} from heavy petroleum feeds, by a process as defined in claim 1, said system comprising at least two riser reactors (1 and 2) wherein, a fresh feed is introduced into the first riser reactor (1), typically, at the bottom section above regenerated catalyst entry zone through a feed nozzle (3), and at the end of the first riser reactor (1), the spent catalyst is quickly separated from hydrocarbon product vapors using separating devices (4) and subjected to

multistage steam stripping to remove any entrained hydrocarbons, and a conduit (5) feeds a part of the said stripped catalyst into a regenerating apparatus (7) and the other part of the stripped catalyst from the conduit (5) travels through another conduit (6) into a mixing vessel (10); and thereafter, the mixed catalyst from the mixing vessel (10) travels through a conduit (19) and is fed to the bottom of the first riser reactor (1), the hydrocarbon product vapors from the first riser reactor (1) which are separated from the catalyst in the separating devices (4) are fed to a vacuum or atmospheric distillation column (13) through conduit (12) whereby the first cracked hydrocarbon products are separated into a first fraction comprising hydrocarbons having boiling points less than or equal to 370°C and a second fraction comprising uncracked hydrocarbons with boiling points greater than or equal to 370°C; the said second fraction comprising uncracked hydrocarbon products is fed through feed nozzle (16) into the bottom of second riser reactor (2) above the regenerated catalyst entry zone, and the regenerated catalyst from the regenerating apparatus (7) is fed to the bottom of the second riser reactor (2) through a conduit (9), and subsequently, the hydrocarbon products of the second riser reactor (2) are separated from the catalyst in separating devices (11), and the cracked products of the second riser reactor (2) along with the products of the first fraction of the first riser reactor (1) comprising hydrocarbons with boiling points less than or equal to 370°C are fed to a main fractionator column (15) which separates the said products into dry gas, LPG, gasoline, heavy naphtha, light cycle oil, heavy cycle oil, and slurry oil, and the entire heavy cycle oil and full or part of the slurry oil consisting mainly of hydrocarbons with boiling points greater than or equal to 370°C are recycled back to the second riser reactor (2) through a separate feed nozzle (17) located at a point lower than the position of introduction of main feed, and the feed and cracked product vapors travel along with the catalyst, into the reactor wherein the spent catalyst separated from product vapors of the second riser reactor (2) in separating devices and the spent catalyst is subjected

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to multistage steam stripping for removal of entrained hydrocarbons and the stripped catalyst travels through a conduit (18) into the regenerating apparatus (7), wherein the coke on catalyst is burnt in the presence of air and/or oxygen containing gases at high temperature, and the flue gas from regeneration is separated from the entrained catalyst fines in separating devices (23) and the flue gas leaves from top of the regenerating apparatus (7) through a conduit (22) for heat recovery and venting through stack; the hot regenerated catalyst is withdrawn from the regenerating apparatus (7) and divided into two parts, one going to the mixing vessel (10) through the conduit (8) and the other directly to the bottom of the second riser reactor (2), and the mixed catalyst from the mixing vessel (10) is fed through the conduit (19) to the inlet of the first riser reactor (1), controlling the catalyst bed level in the individual or common stripper, the catalyst circulation rate from the common regenerator and the quantity of the spent and regenerated catalyst entering into the mixing vessel (10) using slide valves placed on the conduits and thereby producing high yield of middle distillate products.

At the bottom 'Y' section of both the risers (1&2), steam is used to lift the catalyst in upward direction upto the feed entry zone. Also steam is used in the feed nozzles (3,16 &17) for atomization and dispersion of the feed. The quantity of the steam flow into the respective risers (1&2) are varied depending on the feedstock quality and the desired velocity in the risers.

As an example, the system designed to practice the process of the invention has been described employing only two riser reactors. It is pertinent to note that in practice, riser reactors of desired number may be connected to the second riser reactor so that the unconverted hydrocarbons obtained from the second riser may be further treated in accordance with the process described herein above and

eventually, substantially the pure middle distillate products may be obtained in high yield from the original feed.

In catalytic cracking processes using zeolite based catalyst, the reactions proceed sequentially. High boiling large feed molecules first enter the catalyst through relatively large pores which allows pre-cracking to form intermediate middle distillate range molecules which are further cracked to lighter molecules corresponding to Dry gas, LPG and Gasoline. Ideally, middle distillate yield can be increased, if it's cracking to lighter products is restricted. Any attempt in this regard is likely to reduce the conversion, resulting in higher yield of unconverted products. Conventionally, recycling of unconverted fraction has been practiced to improve the overall conversion. The severity required for cracking of the unconverted recycled fraction is adequate to produce significant quantity of gasoline and LPG by over-cracking of middle distillate range product. It also promotes hydrogen transfer reactions producing aromatics in middle distillate range products and therefore, deteriorates the cetane quality. To summarize, it may be noted that maximization of intermediate product middle distillate is more challenging as compared to maximization of gasoline.

In distinction to other prior art processes, the present invention provides a process for producing maximized quantity middle distillate through catalytic cracking of heavy hydrocarbon fractions employing multiple risers. The applicants realized that the middle distillate selectivity is higher only at lower conversion. In fact, the ratio of yield of Total Cycle Oil (TCO:150-370°C) to the sum of other products, (such as, dry gas, LPG, gasoline and coke) increases as the conversion reduces. Moreover, riser temperature has dramatic impact on the selectivity. At same conversion, the applicants have found that middle distillate selectivity improves significantly as riser temperature is reduced. The applicants have also investigated the role of coke on regenerated catalyst (CRC) and

discovered that there is an optimum CRC for maximum yield of TCO (Ref.: Ind. Chem. Res., 32, 1081, 1993). Finally, the applicants have arrived at some specific conditions (comprising of very low riser temperature, low contact time, low catalyst oil ratio, higher CRC, etc.) and type of the catalyst with which yield of TCO is maximized.

According to the present invention, petroleum feed stocks such as Vacuum Gas Oil (VGO), Coker fuel oil, Coker/Visbreaker heavy gas oil, Hydrocracker bottom, etc. is catalytically cracked in presence of solid zeolite catalyst with or without selective acidic bottom cracking components in multiple riser-reactors. The feed is first preheated at a temperature in the range of 150-350°C and then injected to pneumatic flow riser type cracking reactor with residence time of 1-8 seconds and preferably of 2-5 seconds. At the exit of the riser, hydrocarbon vapors are quickly separated from catalyst for minimizing the over cracking of middle distillate to lighter products.

The product from the first riser is separated in a fractionator to at least two streams, one comprising hydrocarbons having boiling below 370°C and the other comprising hydrocarbons having boiling points greater than 370°C. The removal of hydrocarbons having boiling points less than or equal to 370°C products reduces the chance of over-cracking of middle distillate range molecules to lighter products. The unconverted fraction comprising hydrocarbons having boiling points greater than or equal to 370°C fraction from the first riser is pre-heated and then injected to the second riser reactor with residence time of about 1-12 seconds and preferably in the range of about 4-10 seconds, through the feed nozzles located at a higher elevation. In the second riser, the regenerated catalyst is contacted with the recycle stream of unconverted heavy hydrocarbons from the second riser at a relatively lower elevation of the riser. This allows preferential cracking of the recycle components under high severity conditions

(e.g., higher temperature, higher dynamic activity of the catalyst owing to low coke on regenerated catalysts) at the bottom of second riser. Typically, recycle ratio is maintained in the range of 0-50% of the feed throughput in the second riser.

Steam and/or water, in the range of 1-20 wt% of feed is added for dispersion and atomization in both the risers depending on type of feedstock. The desired velocity in the risers, especially in the first riser is adjusted by addition of steam.

The hydrocarbon product vapor from the second riser is quickly quenched with water/other hydrocarbon fraction and separated for minimizing the post riser non-selective cracking. The product from the second riser and the product boiling below 370°C from the first riser are separated in a common fractionator into several products, such as Dry gas, LPG, Gasoline, Heavy naphtha, Light Cycle Oil and cracked bottom. Part of the unconverted bottom product (370°C+ fraction) from the second fractionator is recycled to the second riser and remaining part is sent to rundown after removal of catalyst fines.

The spent catalyst with entrained hydrocarbons from the riser exit is then passed through a common or separate stripping section where counter current steam stripping of the catalyst is carried out to remove the hydrocarbon vapors from the spent catalyst. The catalyst residence time in the strippers is required to be kept in the lower side of preferably less than 30 seconds. This helps to minimize undue thermal cracking reactions and also reduces the possibility of over-cracking of middle distillate range products. Stripped catalyst is then passed to a common dense or turbulent fluidized bed regenerator where the coke on catalyst is burnt in presence of air and/or oxygen containing gases to achieve coke on regenerated catalyst (CRC) of lower than 0.4 wt% and preferably in the range of about 0.1 - 0.3 wt%. A part of the regenerated catalyst is directly circulated to

the second riser reactor via standpipe / slide valve at a temperature of 600 - 750°C.

As mentioned earlier, there is an optimum CRC at which maximum TCO yield is obtained. In order to extract maximum TCO from the first riser, CRC is required to be maintained at relatively higher level, in the range of 0.2– 0.8 wt% depending on catalyst and operating conditions. In the second riser, the desirable CRC is relatively lower (in the range of 0.1 – 0.3 wt%) in order to utilize the full activity potential of the catalyst. Also the temperature of the regenerated catalyst entering to the two risers are different. The lower temperature and higher CRC of the catalyst entering to the first riser is achieved by mixing a part of the stripped catalyst from the first riser / common stripper with regenerated catalyst in a separate vessel equipped with fluidization steam and circulating the mixed catalyst to the bottom of the first riser via stand pipe / slide valve. The mixed catalyst enters at the bottom of the first riser with a temperature in the range of 450 - 575°C (preferably in the range 475 - 550°C) and CRC of lower than 0.8 wt% (preferably in the range of 0.25 – 0.5 wt% depending on type of catalyst). Another option of controlling the catalyst return temperature in the first riser is to employ catalyst cooler so that catalyst/oil ratio could be controlled almost independently. However, the mixing vessel is preferred since it acts as second stage stripper and helps to adjust the coke level on the catalyst.

Prior to the injection of the 370°C+ fraction of the first riser product, the fresh regenerated catalyst is contacted with the recycle stream of unconverted hydrocarbons from the second riser at a relatively lower elevation of the riser. The recycle components are preferentially cracked at the high severity conditions prevailing in the second riser bottom before the injection of 370°C+ fraction of first riser product. Typically recycle ratio is maintained in the range of 0 – 50% of the second reactor feed throughput depending on the type of the

feed to be processed and the conversion level in both the reactors. If the recycle quantity is less, it may be injected along with the main feed i.e., 370°C+ fraction of first riser product.

In the present invention, the first riser operates in the range of 150 - 350 hr⁻¹ weight hourly space velocity (WHSV), 2 - 8 catalyst to oil ratio, 400 - 500°C riser top temperature to convert the feedstock to selectively cracked product including 35 - 45 wt% min. TCO yield and 40 - 60 wt% 370°C+ (bottom) yield. The second riser operates in the range of 75 - 275 hr⁻¹ WHSV, 4 -12 catalyst to oil ratio and 425 -525°C riser top temperature. The absolute pressure in both reactors are 1 - 4 kg/cm² (g). Steam and / or water, in the range of 1 - 20 wt% of feed is added not only for dispersion and atomization of feed but also to attain the desired fluidization velocity in the risers, especially in the first riser bottom. It also helps in avoiding the coke formation or catalyst agglomeration.

Comparison of major process conditions of the process of the present invention with conventional FCC & multi stage process is shown below :

Table – 1

	Multistage process of the present invention				FCC Process
	first reactor		second reactor		
	Range	Preferred Range	Range	Preferred Range	Range
WHSV, hr ⁻¹	150 – 350	200– 300	75 – 275	120 – 220	125 -200
Catatyst/Oil ratio (w/w)	2 – 8	3 – 5	4 –12	5 – 8	4 - 8
Riser temp., °C	400 – 500	425 - 475	425 – 525	460 – 510	490- 540
Steam injection, wt% of feed	1 - 20	8 - 12	1 – 20	4 – 8	0 - 10

Use of multiple riser concepts is not new, as each researcher has employed it for different purposes. The present invention utilizes dual or multiple riser systems for exclusive maximization of middle distillate products. Being an intermediate product, middle distillate range molecules have a tendency to undergo further cracking. There is always a trade off between maximization of an intermediate range product and minimization of bottom unconverted part. This invention includes the sequence of operation and operating conditions for control of over-cracking of middle distillate in the first riser and upgradation of heavier molecules to middle distillate in the second riser. This invention provides a novel scheme for operation of two or multiple risers at entirely different operating conditions with a common regenerator. Use of so much lower temperature cracking is unusual so far. However, the applicants have found that reaction temperature has a predominant effect on the over cracking of middle distillate range products. For example, at 40 wt% of 370°C- conversion, the wt% yield ratio of TCO and all other products, (i.e., Dry Gas, LPG, Gasoline & Coke) except TCO and bottom (subsequently referred as TCO/Rest ratio) are in the range of about 3.0 – 3.5 and about 1.5 – 1.8 at reaction temperatures of 425°C and 490°C respectively. The difference in the above ratio is narrowed down as the conversion increases (Figure-3).

Therefore, for maximizing TCO, low reaction temperature and catalyst to oil ratio as well as low catalyst activity is desirable. The applicants identified that lower catalyst / oil ratio (2 - 8) and higher WHSV of (150 - 350 hr⁻¹) along with lower riser temperature in the first riser of the process of the present invention are very important to achieve very low degree of over cracking for producing maximum middle distillate range components. The applicants also observed that the TCO/Rest ratio is significantly affected by the 370°C- conversion level. For example, for a given catalyst and reaction temperature, if 370°C- conversion is 40%, the TCO/Rest ratio is as high as 3.2 which comes down to about 1.3 when

370°C - conversion is increased to 70%. This shows that restricting the conversion in the first stage riser upto 40 – 45% is very important to maximize the yield of middle distillate.

In the second riser, the operating conditions need to be different for upgradation of relatively less crackable heavy material to lighter products. However, undue increase in severity parameters will lead to conversion to LPG and Gasoline. The applicants have discovered that operation at an intermediate severity as compared to gasoline maximization mode FCC operation is absolutely necessary. The applicants have also found that in order to reduce the yield of unconverted bottom and improve the middle distillate selectivity, recycle at a lower elevated entry point at the bottom of the second riser is very much effective. This allows the cracking of the recycled heaviest fraction in presence of regenerated catalyst at relatively higher temperature and lower CRC which improves the dynamic activity of the catalyst and offers maximum cracking of the recycled feed. After cracking of the recycled part, the catalyst temperature comes down due to utilization of part of the heat for vaporization and endothermic cracking reactions of the recycled feed. Also, the coke on catalyst increases which essentially blocks some of the active sites and thereby reduces the dynamic activity of the catalyst. The contacting of catalyst having relatively lower temperature and higher coke on catalyst with the main feed comprising the fraction of the first riser of hydrocarbons with boiling points greater than or equal to 370°C, assists to improve the selectivity of middle distillate range products out of the second riser. This contacting pattern is unique and highly effective in increasing the overall yield of the middle distillate and reducing yield of the unwanted slurry oil.

In the present invention, the delta coke (defined as the difference in coke content of spent and regenerated catalyst) is low due to lower coke make in the extremely low severity cracking in the first riser which is expected to keep the

regenerator temperature at relatively lower level as compared to the conventional FCC operation using similar type of feedstocks. However, overall lower catalyst oil ratio is likely to compensate this effect and thereby maintain the regenerator temperature at least to the same level as that of conventional FCC as required for burning of coke on catalyst.

Further details of feedstock, catalyst, products and operating conditions of the process of the present invention are described below:

Feed Stock:

Feed stock for the present invention includes hydrocarbon fractions starting from carbon no. 20 to carbon no. 80. The fraction could be straight run light and heavy Vacuum Gas Oil, Hydrocracker bottom, Heavy Gas Oil fractions from Hydrocracking, FCC, Visbreaking or Delayed Coking. The conditions in the process of the present invention are adjusted depending on the type of the feedstock so as to maximize the yield of middle distillate. Details of the feedstock properties are outlined in the examples given hereinbelow.. The above feed stock types are for illustration only and the invention is not limited in any manner to only these feed stocks.

Catalyst:

Catalyst employed in the process of the present invention predominantly consists of Y-zeolite in rare earth ultra-stabilized form. Bottom cracking components consisting of peptized alumina, acidic silica alumina or γ -alumina or a mixture thereof are also added to the catalyst formulation to produce synergistic effect towards maximum middle distillate under the operating conditions as outlined above. It may be noted that both the first and second stage risers are charged with same catalyst. The pore size range of the active components namely, Re-USY zeolite and bottom selective active materials are in the range of 8 – 11 and

50 – 1000 angstrom respectively. The typical properties of the Y-zeolite based catalyst are given in Table-2.

Table - 2

Surface Area, m ² /g,	Fresh	110 – 180
	Steamed	100 – 140
% Crystallinity	Fresh	10 – 15
	Steamed	8 – 12
Unit Cell Size, °A	Fresh	24.35 – 24.75
	Steamed	24.2 – 24.6
Micro-pore area, m ² /g,	Fresh	65 – 100
	Steamed	60 – 90
Meso-pore area, m ² /g,	Fresh	45 - 80
	Steamed	40 - 50
Pore volume, cc/gm		0.25 – 0.38

The active components in the process of the present invention catalyst are supported on inactive materials of silica/alumina/silica-alumina compounds including kaolinites. The active components could be mixed together before spray drying or separately binded, supported and spray-dried using conventional spray drying technique. The spray-dried micro-spheres are washed, rare earth exchanged and flash dried to produce finished catalyst particles. The finished micro-spheres containing active materials in separate particles are physically blended in the desired composition. The preferred range of physical properties of the finished fresh catalyst as required for the process of the present invention:

Particle size range, micron : 20-120

Particle below 40 microns, wt% : < 20

Average particle size, micron : 50-80

Average bulk density, micron : 0.6 – 1.0

Typically, the above properties and other related physical properties, e.g., attrition resistance, fluidizability etc. are in the same range as used in the conventional FCC process.

Products:

The main products in the process of the present invention is the middle distillate components namely, Heavy Cracked Naphtha (HCN : 150 – 216°C) and Light Cycle Oil (LCO : 216 – 370°C). The sum total of these two fractions which is called as Total Cycle Oil (TCO : 150 – 370°C) is obtained with a yield upto 50 - 65 wt% of the feed. The other useful products of the process are LPG (5 - 12%) and Gasoline (15 - 25 wt%). Range of other product yields from first and second stage risers are summarized in Table - 3:

Table – 3

	Yield, wt% of feed		
	From first reactor	From second reactor	Combined yield from both first & second
Dry Gas ($C_1 + C_2$)	0.1 – 0.35	1-1.5	0.5 – 1.5
LPG ($C_3 + C_4$)	3 – 4	8 – 12	5 – 12
Gasoline ($C_5 - 150^0C$)	10 – 15	25 – 30	15 – 30
Heavy Naphtha, (150–216 ⁰ C)	8 – 10	10 – 13	10 – 15
Light Cycle Oil, (216–370 ⁰ C)	35 – 45	25 – 35	40 – 50
Total Cycle Oil (150–370 ⁰ C)	45 – 50	30 – 40	50 – 65
Bottom (370 ⁰ C+)	40 – 60	10 – 20	5 – 15
Coke	1 – 3	2 – 5	2 – 4

The invention and its embodiments are described in further detail hereunder, with reference to the following examples, which should not be construed to limit the scope of the invention in any manner. Various modifications of the invention that may be apparent to those skilled in the art are deemed to be included within the scope of the present invention.

Example-1

Yield of middle distillate at different conversions in conventional FCC operation

This example illustrates the change in yield of the middle distillate product (TCO) at different conversion levels under conventional FCC conditions. -216°C conversion is defined as the total quantity of products boiling below 216°C including Coke. Similarly -370°C conversion is defined as the total quantity of products boiling below 370°C including Coke. The experiments were conducted in standard fixed bed Micro Activity Test (MAT) reactor described as per ASTM D-3907 with minor modifications indicated subsequently as modified MAT. The catalyst to be used is first steamed at 788°C for 3 hours in presence of 100% steam. The physico-chemical properties of the feed used in the modified MAT reactor are given in the Table – 4 & 5.

Table – 4

Density @ 15°C, gm/cc	0.8953
CCR, wt%	0.32
Sulfur, wt%	1.12
Basic Nitrogen, PPM	366
Paraffins, wt%	44.4
Naphthenes, wt%	18.1
Aromatics, wt%	37.6

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Nickel, PPM	< 1
Vanadium, PPM	< 1

The runs were taken at a reaction temperature of 495°C, feed injection time of 30 seconds with WHSV in the range of 40 – 120 hr⁻¹. Catalysts used in this example are catalyst A & B which are commercially available FCC catalyst samples having properties as shown in the Table-6.

Table – 5

ASTM Distillation (D1160) :	
Volume %	Temperature, °C
IBP	299
5 / 12 / 15 / 20 / 30 / 40	342 / 358 / 371 / 381 / 401 / 418
50 / 60 / 70 / 80 / 90 / 95	432 / 444 / 458 / 474 / 497 / 515
FBP	550

Table – 6

		Catalyst – A	Catalyst – B
Surface Area, m ² /gm	Fresh	170103	272 208
	Steamed		
Pore Volume, cc/gm		0.22	0.26
ABD, gm/cc		0.81	0.79
Crystallinity, %	Fresh	18.9	27.7
	Steamed	-	23.2
UCS, °A	Fresh	24.61	24.56
	Steamed	24.32	24.31

Chemical Analysis, wt%		
Al ₂ O ₃	56.5	30.85
Re ₂ O ₃	1.44	1.03
Fe	0.49	0.53
APS, microns	74	77

The product yields along with conversions are given in Table-7 wherein it is observed that as in both -216⁰C and -370⁰C conversion increases, TCO yield increases upto an optimum value and thereafter, it reduces with increase in conversion. TCO being an intermediate product, undergoes further cracking as reaction severity increases. Therefore, in order to maximize TCO yield, the over-cracking is to be restricted.

Table – 7

Product Yield, wt%	Catalyst A			Catalyst B			
W/F, Min.	0.51	0.62	0.94	0.44	0.51	0.63	0.94
Hydrogen	0.018	0.021	0.041	0.025	0.025	0.033	0.046
Dry gas	0.44	0.56	1.14	0.59	0.64	0.86	1.46
LPG	7.33	8.82	13.61	6.18	6.97	10.09	12.34
Gasoline	19.32	23.43	30.78	17.20	20.50	25.03	30.94
TCO	40.09	41.53	37.79	36.33	37.97	39.94	37.67
Bottom (370 ⁰ C+)	31.81	24.52	14.25	38.73	32.82	22.80	14.92
Coke	0.99	1.13	2.39	0.95	1.08	1.25	2.61
-216 ⁰ C	40.17	47.50	62.45	34.96	40.34	49.98	60.99
Conversion							
-370 ⁰ C	68.19	75.48	85.75	61.27	67.18	77.20	85.08
Conversion							

Example-2**Effect of reaction temperature on middle distillate yields at same conversion**

This example illustrates the effect of reaction temperature on the yield of middle distillate at a given -216°C conversion. The experiments were conducted in the modified MAT reactor with the same feed as mentioned in Example-1, at two different temperatures, viz., 425°C and 495°C . Catalyst employed here is catalyst C which is commercially available FCC catalyst of following properties as shown in the Table – 8.

Table – 8

		Catalyst – C
Surface Area, m^2/gm	Fresh	172
	Steamed	119
Pore volume, cc/gm		0.32
Crystallinity, %	Fresh	13.80
	Steamed	10.20
UCS $^{\circ}\text{A}$	Fresh	24.55
	Steamed	24.31
Chemical Analysis, wt%		
RE ₂ O ₃		0.69
Al ₂ O ₃		36.40
Na ₂ O		0.11
Particle size, micron / wt%		
-20 / -40 / -60 / -80 / -105 / -120		3 / 16 / 32 / 56 / 77 / 86
APS, micron		76

Table – 9

Temperature, °C →	425		495	
-216°C conversion, wt%	30	50	30	50
W/F, Min.	1.1	2.7	0.10	0.5
<u>Yield Pattern, wt%</u>				
Dry gas	0.20	0.42	0.38	0.56
LPG	4.10	9.1	5.07	10.72
Gasoline	14.94	23.52	16.00	24.58
Heavy naphtha	9.50	14.27	7.11	11.20
LCO	28.68	32.00	25.80	24.50
TCO	38.18	46.27	32.91	35.70
Bottom (370°C+)	41.32	18.00	44.20	25.40
Coke	1.26	2.69	1.44	2.94
370 °C Conversion	58.68	82.00	55.80	74.60
TCO /Rest	1.86	1.29	1.43	0.92

The conversion was varied by changing W/F ratio. The product yields are compared at same -216°C conversion but at different temperatures. It is noted from Table-9 that at higher temperature, TCO yield and more importantly the TCO/Rest ratio (the ratio of TCO yield and yield of other products e.g., Dry gas, LPG, Gasoline and Coke except bottom and TCO) are much lower in case of higher reaction temperature. For example, at a given -216°C conversion, TCO yield at 425°C temperature is about 6 - 10% higher than that at 495°C. The other significant point is that at low temperature of 425°C, it has been possible to get 46% TCO yield (per pass) at 50% -216°C conversion. Similarly, there is a significant improvement in TCO/Rest ratio for 425°C as compared to that of 495°C at same conversion. This clearly demonstrates that in order to conserve middle distillate range molecules, low reaction temperature is essential.

Example-3

First stage riser cracking conditions

This example illustrates the significance of first stage riser cracking conditions e.g., temperature, catalyst/oil ratio and conversion on the yield of middle distillate and other products while employing commercially available FCC catalysts A and C, properties of which are described in Example-1 & 2 respectively. The tests were conducted in modified fixed bed MAT unit with same feed as described in Example-1. Yield data were generated at different conversion level for the catalysts as indicated above and the yields of different products were obtained. TCO/Rest ratios at different conversion levels are plotted in Figure-3, from which it is observed that for both the catalysts, the TCO/Rest ratio increases as the -370°C conversion is reduced. Therefore, it is important to note that the per pass -370°C conversion in the first stage riser should be kept below 45% and preferably below 40%.

From Figure-3, it is also observed that the TCO/Rest ratio is a strong function of the reactor temperature for a given conversion and catalyst. For example, with catalyst C, while reducing reaction temperature from 490 to 425°C , the TCO/Rest ratio is increased from 3.4 to 3.75 at about -370°C conversion level of 40%. This clearly shows that for the first stage cracking, the reaction temperature should be kept lower, preferably in the range of 425 – 450°C .

Example - 4

Catalyst characteristics for middle distillate maximization

One of the important observation as illustrated in Example-3, is that for maximization of middle distillate yield, it is necessary to restrict the per-pass conversion within 40 – 45% and operate the first stage riser at lower reaction temperature. The low reaction temperature coupled with high coke on regenerated catalyst leads to lower dynamic activity of the catalyst. Therefore,

the desired catalyst should have high intrinsic activity. However, the problem is that high active catalysts are not usually diesel selective. In this example, we illustrate the importance of catalyst characteristics to obtain higher yield of middle distillate out of the dual / multi – stage risers.

MAT activity is measured in ASTM MAT unit using a standard feedstock and defined as the wt% of products boiling below 216°C including coke at ASTM conditions. All other experiments were conducted at the temperature of 425°C in the modified MAT reactor with the same feed as described in Example-1 and different catalysts. The important properties of the catalysts and the yield / conversion data are compared in Table-10.

Table-10

	Catalyst – A	Catalyst-C	Catalyst-D	Catalyst-E
Surface Area, m ² /gm	103	119	110	20
Zeolite Area, m ² /gm	59	80	62	-
Rare earth content, wt%	1.44	0.69	1.40	-
Matrix Area, m ² /gm	44	39	48	-
Zeolite / Matrix ratio	1.34	2.05	1.29	-
MAT Activity	71.38	74.02	70.19	13.55
TCO Yield at 40% -370°C Conversion	31.00	32.01	30.90	31.20
TCO yield/Rest ratio at 40% -370°C conversion	3.44	4.00	3.39	3.30
W/F for 40% -370°C conversion	0.22	0.25	0.22	3.5

Table -11

	Catalyst-A	Catalyst-C	Catalyst-D
TCO Yield at 80% -370°C Conversion	38.45	34.78	43.0
TCO yield/Rest ratio at 80% -370°C conversion	0.95	0.80	1.08

It is seen that the zeolite/matrix ratio, TCO yield at 40% -370°C conversion, TCO / Rest ratio are in the order of $C > A > D$. In catalyst C, the available active matrix is adequate to crack the large molecules which are crackable under the prevailing operating conditions but it requires slightly higher W/F ratio. Higher zeolite quantity is also synergistically taking part in the over all cracking activity but the conversion of middle distillate to lighter products is not increasing corresponding to higher zeolite content due to lower temperature. However for catalyst-E, whose activity is extremely low, at 40% of -370°C conversion, both TCO yield and TCO/Rest ratio is comparable to those with the higher active catalysts. But W/F ratio required to achieve 40% -370°C conversion is much higher which is difficult to achieve. At comparable W/F ratio, -370°C conversion will be very low, producing very low amount of TCO. Therefore, such low active catalyst is not useful for producing maximum distillate.

Experiments with catalysts A, C & D at a reaction temperature of 495°C corresponding to the second riser conditions were taken and the TCO yield and TCO/ Rest ratio are compared at -370°C conversion of 80% in Table-11. Both the TCO yield and TCO/ Rest ratio are found to be in the order of $D > A > C$. It may be noted that the zeolite / matrix ratio is just in the reverse order i.e., $C > A > D$. The higher quantity of zeolite as well as the high zeolite/matrix ratio in catalyst C, is resulting in overcracking of middle distillate range molecules into lighter products. For a given -370°C conversion, the -216°C conversion is much higher for catalyst C. It is quite clear that the catalyst which is supposed to be the best in the first riser conditions, may not be that much good for the second riser conditions as far as TCO maximization is concerned. This demonstrates that in order to achieve maximum TCO and minimum Bottom yield, some optimization of the catalyst properties is essential.

Example- 5**Impact of basic nitrogen compound on middle distillate yield**

It is generally conceived that low activity of the catalyst is desirable for maximum distillate yield. Basic nitrogen compounds present in feed stock interact with the catalyst at reaction conditions leading to loss of the active acid sites and hence decrease of catalyst activity. Two feed stocks were prepared containing 200 and 700 PPM pyridine respectively. The experiments were conducted in the modified MAT reactor with catalyst C using the same feed stock as mentioned in Example-1, but containing different PPM of pyridine, at the temperature of 425°C. The conversion and yield data are shown in Table-12.

Table-12

	Feed without Pyridine	Feed containing 200 PPM Pyridine	Feed containing 700 PPM Pyridine
-216°C conversion at 40% -370°C conversion	13.50	14.15	13.99
TCO Yield at 40% -370°C conversion	32.00	30.90	29.98
TCO/Rest ratio at 40% -370°C conversion	4.00	3.39	3.00
W/F to achieve 40% - 370°C conversion	0.25	0.30	0.38

It is observed that both TCO and TCO/Rest ratio are decreasing as the feed basic nitrogen content is increasing. However, at 40% -370°C conversion, -216°C conversion is increasing with increase in basic nitrogen in feed upto 200 PPM after which it reduces marginally at 700 PPM of pyridine in feed. This is due to the irreversible adsorption of the nitrogenous basic compounds leading to preferential destruction/poisoning of the strong acid sites, which are responsible for heavy molecule cracking. This is reflected in the higher W/F requirement to achieve 40% -370°C conversion. However, so called relatively weaker acid sites which do not get affected by basic nitrogen, helps in cracking of middle distillate

range molecules at higher W/F resulting higher -216°C conversion. In case of 700 PPM pyridine containing feed, even some of the relatively weaker acid sites are getting affected reducing both -216°C and -370°C conversion as compared to the 200 PPM pyridine containing feed case. This example demonstrates that just activity reduction may not lead to higher middle distillate yield.

Example – 6

Impact of cracking conditions for second stage riser operation

This example illustrates the significance of second stage riser cracking conditions e.g., temperature, catalyst/oil ratio and conversion on the yield of middle distillate. The tests were conducted in modified fixed bed MAT unit as described in Example-1, using catalyst C, at the temperature of 425, 490 and 510°C . The feed stock used is 370°C^{+} product obtained from first stage cracking in circulating riser FCC pilot plant, the properties of which is summarized in Table-13. Product yields data were generated at different conversion levels at different temperatures for catalyst C and according the TCO/Rest ratios at different conversion levels are plotted in Figure-4.

Table – 13

Density, gm/cc @ 15°C	0.903
CCR, wt%	0.43
Sulfur, wt%	1.75
Olefins, wt%	Nil
Saturates, wt%	59.0
Aromatics, wt%	41.0

From the Figure-4, it is observed that at a given temperature, the TCO/Rest ratio increases as the -370°C conversion reduces. Also, at a given -370°C conversion, TCO/Rest ratio improves as the reaction temperature reduces. For example, at

about -370°C conversion of about 55%, TCO/Rest ratio increases from 1.22 to 1.34 as the temperature is reduced from 510°C to 490°C . This clearly shows that even for the second stage cracking, the reaction temperature should be kept preferably lower. However, it will also lead to generation of higher quantity of bottom at same W/F ratio. At 425°C , W/F required to crack the $370^{\circ}\text{C}+$ product from first stage cracking along with the recycle stream (unconverted part from the second riser) will be very high and hence difficult to achieve. Another important fact is that the mean average boiling point (MeABP) of second riser combined feed is definitely higher than that of first riser. Operation at lower temperature than the MeABP of the second riser combined feed is not desirable as it will lead to non-selective thermal cracking of the non-vaporized feed producing higher quantity of Coke and Dry gas. Considering these, it has been established that in the second riser, the reaction temperature should be preferably kept in the range of $460 - 510^{\circ}\text{C}$.

Example – 7

Combined effect of two stage cracking on middle distillate yield

In this example, the yields from two stage catalytic cracking for maximization of middle distillate is demonstrated. The experiments have been conducted using catalyst C in continuously circulating fluid bed pilot plant of feed rate 0.75 kg/hr where both the riser and regenerator are operated isothermally. The feed is the same as mentioned in Example-1. After first stage cracking at 425°C , the product is separated into $370^{\circ}\text{C}-$ and $370^{\circ}\text{C}+$ fractions. In the second stage $370^{\circ}\text{C}+$ fraction is cracked at 495°C using the same catalyst as used in the first stage. The product yields from the first and second stage cracking and also the combined yields are given in Table-14.

Table-14

	first stage	second stage	Combined yields
Temperature, °C	425	495	
<u>Yield Pattern, wt%</u>			
Dry gas	0.26	1.28	0.81
LPG	3.37	16.65	10.55
Gasoline	10.65	26.03	21.88
Heavy naphtha	8.54	13.31	14.28
LCO	32.33	19.47	40.73
TCO	40.87	32.78	55.01
370 °C +	43.25	20.44	8.82
Coke	1.70	2.85	2.93

It is clearly seen that the ratio of yield of TCO and the sum of yields of Dry gas, LPG, Gasoline and Coke (TCO/Rest) is very high in case of the first stage cracking which is essentially contributing higher TCO yield for the overall process. For second stage cracking, the TCO/Rest ratio is similar to that of conventional distillate mode FCC unit as the severity required for minimizing the bottom yield is high enough to crack significant portion of TCO produced from heavy molecule cracking.

The yield comparison between single and dual riser cracking at similar -216°C conversion with same catalyst and feed is compared in Table-15. It is seen that for same -216°C conversion, -370°C conversion is much higher resulting about 20% higher yield of TCO in case of two stage cracking. This establishes the workability of the concept of the present invention where process schemes, catalyst and operating conditions are such that TCO over-cracking is restricted

with simultaneous the upgradation of heavy molecules to TCO range molecules. Here, the first riser operates to extract as much TCO as possible while minimizing the yields of lighter products and the second riser is operated to upgrade as much bottom as possible while maximizing the yield of TCO. This process overcomes the trade off between lower bottom yield and higher TCO yield.

Table-15

	Dual riser	Single riser
Temperature, °C	425 & 495	495
Yield Pattern, wt%		
Dry gas	0.81	0.56
LPG	10.55	10.72
Gasoline	21.88	24.58
Heavy naphtha	14.28	11.20
LCO	40.73	24.50
TCO	55.01	35.70
370 °C	8.82	25.40
Coke	2.93	2.94
-216 conversion, wt%	50.45	50.0

Example – 8

Comparison of Micro-reactor & Circulating pilot plant data

This example shows the comparison of individual product yields obtained from Micro-reactor and circulating Pilot Plant using same catalyst and feedstock at similar -216°C conversion range. From the data summarized in Table-16, it is noticed that at similar conversion, there is an excellent match in Gasoline, TCO and bottom yields. The main difference is coming in the yields of Dry gas, LPG

and Coke. This is mainly due to the non-selective thermal cracking reactions occurring at the riser bottom as well as at the end of the riser in the pilot plant. This has resulted relatively higher yield of Dry gas and Coke in the pilot plant riser. This example demonstrates that so far the yields of TCO and un-reacted bottom are concerned, the inferences drawn based on either Micro-reactor or Pilot Plant data are going to be same.

Table-16

	Pilot Plant data		Micro-reactor data	
Feed rate, gm/min	12.9	13.3	-	-
CCR, gm/min	55.5	53.0	-	-
Cat/Oil (w/w)	4.29	3.98	-	-
W/F, min.	-	-	0.609	0.501
Contact time, sec	-	-	30	30
-216 Conversion, wt%	29.86	25.0	29.39	24.93
<u>Product Yields, wt%</u>				
Dry gas	0.62	0.36	0.17	0.13
LPG	8.28	6.29	9.96	8.61
Gasoline	11.82	10.7	12.00	10.65
Heavy Naphtha	7.15	5.92	5.80	4.62
LCO	27.3	26	28.29	26.61
TCO	34.45	31.9	34.09	31.23
370°C +	42.82	49	42.31	48.46
Coke	2.00	1.71	1.46	0.91

Example – 9

Comparison of the yields of present two stage process in present invention, commercial FCCU and two stage hydrocracker

The product yields of the present invention is compared with that of commercial distillate mode FCC and two-stage hydrocracker units in Table-17. The data for the process of the present invention is the combined yield obtained from two stage cracking where the two risers are operated at 425⁰C and 495⁰C respectively.

Table – 17

Product yields, wt% of feed	Distillate mode FCC	Present process	Yields, wt% of feed	Distillate mode Hydrocracker	Present process
Dry gas	2.50	0.78	Dry gas	1.74	0.70
LPG	10.5	10.55	LPG	2.91	9.11
Gasoline (C ₅ -150 ⁰ C)	27.5	21.88	Gasoline (C ₅ -120 ⁰ C)	16.28	12.86
Heavy Naphtha (150-216 ⁰ C)	12.5	14.28	(120-216 ⁰ C) (120-285 ⁰ C)	- 27.91	18.41 -
LCO (216-370 ⁰ C)	30.0	40.73	(216-390 ⁰ C)	-	50.39 -
TCO (150-370⁰C)	42.5	55.01	(120-390⁰C)	73.26	68.80
370 ⁰ C ⁻	12.75	8.82	370 ⁰ C ⁺	5.81	5.85
Coke	4.25	2.93	Coke	-	2.68
-216 ⁰ C conv.	57.25	50.45	-216 ⁰ C conv.	-	-
-370 ⁰ C conv.	87.25	91.18	-370 ⁰ C conv.	94.19	94.15

It is observed that in the process of the present invention, the TCO yield is higher by about 12.50% as compared to the commercial FCC unit. By varying the cut point of TCO from 150 - 370⁰C to 120 - 390⁰C as reported for Hydrocracker unit, and processing the hydrocarbon product vapors having

boiling points greater than or equal to 370°C of the first riser product in the second riser, the yield of TCO increases by about 14 wt% which is only about 5% less than that from the commercial Hydrocracker unit. Also, the conversion of hydrocarbon product vapors having boiling points less than or equal to 370°C is similar to hydrocracker and better than distillate mode FCC unit. This demonstrates that without using external hydrogen and operating under very high pressure, it is possible to produce higher yield of middle distillate product which is close to that from a distillate mode two stage Hydrocracker unit.

Example -10

Comparison of properties of TCO obtained in the process of the present invention with middle distillate products obtained from commercial FCCU and two stage Hydrocracker

The properties of the TCO obtained from the process of the present invention is compared with TCO from commercial distillate mode FCC and Diesel from distillate mode two stage Hydrocracker units which is given in Table-18.

Table -18

	Process of the present invention		Distillate mode FCC	Distillate mode Hydrocracker
	1	2	3	4
	TCO	Middle distillate	TCO	Diesel
TBP cut point, °C	150 - 370	120 - 390	150 - 370	150 - 390
Density @ 15°C, gm/cc	0.8793	0.8863	0.8654	0.835
Pour point, °C	0.7	36	0 - 2	6 - 10
Kinematic Viscosity @ 50°C, CST	2.20	7.00	2.7	9.0

PONA Analysis, wt%				
Olefins	19.97	6.82	18.6	Nil
Saturates	24.64	49.26	22.1	91
Aromatics	55.39	43.92	59.3	9
Cetane no.	36.22	38.39	28 - 30	63

Expectedly, the quality of Diesel range product from Hydrocracker is much superior in terms of cetane no., olefin and aromatics contents etc. than the cracked products without using hydrogen. Mainly, the high aromatics content in cracked middle distillate product contribute to poor cetane quality. However, the viscosity and the pour point of Hydrocracker Diesel is poor as compared to TCO from conventional FCC unit or the process of the present invention. From column 1 & 3, it is seen that the cetane no. of TCO obtained from the present process is higher by 6 units than TCO from conventional distillate mode FCCU. All other properties including the pour point are almost in the same range. In column 2, the properties of the product fraction of 120–390°C range for the present process is listed. While cetane no. of this fraction is further higher, the pour point as well as the viscosity is very high. This has been mainly contributed by the hydrocarbon fraction of 370 – 390°C cut from the first riser product of the present process. The pour point as well as the viscosity of this product fraction is very high and hence its inclusion in the middle distillate product is not desirable. If we take the 120 – 370°C cut from the first riser product and the 120 – 390°C cut from the second riser (while processing the unconverted 370°C+ part of the first riser product into the second riser), the pour point and the kinematic viscosity @ 50°C become 0.95°C and 2.44 CST respectively, which are almost same as that of 150 – 370°C product of the present invention as shown in the column 1 of Table- 18. Additionally, by this approach, the yield of the middle distillate increases from about 55 wt% to 63.6 wt% without any adverse impact on flash point.

We Claim

1. A multi stage selective catalytic cracking process for producing high yield of middle distillate products having carbon atoms in the range of about C_8 to C_{24} , from heavy hydrocarbon feed stocks in the absence of added hydrogen, said process comprising the steps of :
 - i) contacting preheated feed stock with a mixed catalyst in a first riser reactor under catalytic cracking conditions including catalyst to oil ratio of 2 to 8, WHSV of $150-350 \text{ hr}^{-1}$, contact period of about 1 to 8 seconds and top temperature in the range of about 400°C to 500°C to obtain first cracked hydrocarbon products;
 - ii) separating the first cracked hydrocarbon products from the first riser reactor in a vacuum or atmospheric distillation column into a first fraction comprising hydrocarbons with boiling points less than or equal to 370°C and a second fraction comprising unconverted hydrocarbons with boiling points greater than or equal to 370°C ;
 - iii) cracking the unconverted second fraction from the first riser reactor comprising hydrocarbons having boiling points greater than or equal to 370°C , in the presence of regenerated catalyst, in a second riser reactor operating under catalytic cracking conditions including WHSV of $75-275 \text{ hr}^{-1}$, catalyst to oil ratio of 4-12 and riser top temperature of $425 - 525^\circ\text{C}$ to obtain second cracked hydrocarbon products;
 - iv) separating the catalytically cracked products from the second riser reactor alongwith the cracked products comprising hydrocarbons having boiling points less than or equal to 370°C , from the first riser reactor in a main fractionating column to yield cracked

products comprising dry gas, LPG, gasoline, middle distillates, heavy cycle oil and slurry oil;

- v) recycling the entire heavy cycle oil comprising hydrocarbons having boiling points in the range of 370°C to 450°C and full or part of the slurry oil having boiling points greater than or equal to 450°C, into the second riser reactor at a vertically displaced position lower than the position of introduction of the main feed comprising bottom unconverted hydrocarbon fraction having boiling points greater than or equal to 370°C from the first riser reactor to obtain middle distillate products comprising hydrocarbons having carbon atoms in the range of C₈ - C₂₄ ranging from about 50 to 65 wt % of the feed stock,
 - vi) optionally, recycling the fraction of unconverted hydrocarbons with boiling points greater than or equal to 370°C, obtained in step (iv) in riser reactors by repeating steps (iii) to (iv) to obtain substantially pure middle distillate products.
2. A process as claimed in claim 1 wherein, the feed stock is selected from petroleum based heavy feed stock such as vacuum gas oil (VGO), visbreaker/coker heavy gas oil, coker fuel oil and hydrocracker bottom, etc.
 3. A process as claimed in claim 1 wherein the feed stock is preheated at a temperature in the range of 150-350°C and then injected to pneumatic flow riser type cracking reactor
 4. A process as claimed in claim 1 wherein, the mixed catalyst is obtained from an intermediate vessel that mixes the spent catalyst from the

common stripper or preferably first stripper with the regenerated catalyst from the common regenerator and charges the mixed catalyst with coke content in the range of about 0.2 to 0.8 wt% of catalyst to the bottom of the first riser at a temperature of 450 - 575°C.

5. A process as claimed in claim 1 wherein the cracked hydrocarbon vapor products from the first and second risers are quickly separated from respective spent catalysts using separating devices to minimize the over cracking of middle distillate range products into undesirable lighter hydrocarbons.
6. A process as claimed in claim 1 wherein the spent catalysts from the first and second riser reactors are passed through respective dedicated catalyst strippers or a common stripper to render the catalysts substantially free of from entrained hydrocarbons.
7. A process as claimed in claim 1 wherein the regenerated catalyst with coke content of less than 0.4 wt% is obtained by burning a portion of the spent catalyst from the first stripper, the spent catalyst from the second stripper or the common stripper in a turbulent or fast fluidized bed regenerator in the presence of air or oxygen containing gases at a temperature in the range of about 600°C to 750°C.
8. A process as claimed in claim 1 wherein the catalyst between the fluidized bed riser reactors, strippers and the common regenerator is continuously circulated through standpipe and slide valves.
9. A process as claimed in claim 1 wherein the critical catalytic cracking conditions in the first reactor including mixed regenerated catalyst result

in very high selectivity of middle distillate range products and conversion of hydrocarbon products of boiling point less than or equal to 370°C at lower than 50 wt% of the fresh feed.

10. A process as claimed in claim 1 wherein the catalyst comprises a mixture of commercial ReUSY zeolite based catalyst having fresh surface area of 110-180 m²/gm., pore volume of 0.25-0.38 cc/gm and average particle size of 60-70 micron along with selective acidic bottom upgrading components in the range of about 0-10 wt%.
11. A process as claimed in claim 1 wherein the unconverted heavy hydrocarbon fraction from second riser recycled into the second riser ranges from about 0-50 wt% of the main feed rate to the second riser, depending on the nature of the feedstock and operating conditions kept in the risers.
12. A process as claimed in claim 1 wherein amount of steam for feed dispersion and atomization, catalyst lifting at the riser bottom in the first and the second riser reactors is in the range of 1-20 wt% of the respective total hydrocarbon feed depending on the quality of the feedstock.
13. A process as claimed in claim 1 wherein the spent catalyst resides in the stripper for a period of upto 30 seconds.
14. A process as claimed in claim 1 wherein the regenerated catalyst entering at the bottom of the second riser reactor has coke of about 0.1-0.3 wt% at a temperature of about 600-750°C and is lifted by catalytically inert gases.

15. A process as claimed in claim 1 wherein the combined Total Cycle Oil (150-370°C) product which is a mixture of Heavy naphtha (150-216°C) and Light cycle oil (216- 370°C), has higher cetane number than that from conventional distillate mode FCC unit and other properties such as specific gravity, viscosity, pour point, etc. are in the same range as that of commercial distillate mode FCC unit.
16. A process as claimed in claim 1 wherein changing the cut point of the TCO from the first riser to 120-370°C, processing 370°C+ part of the first riser product in the second riser, and changing the cut point of TCO from second riser to 120-390°C, the yield overall combined TCO product increases by 8-10 wt% and the combined TCO product has the same properties but improved cetane number as that of TCO from commercial distillate mode FCC unit.
17. A process as claimed in claim 1 wherein the Total Cycle Oil comprises a mixture of heavy naphtha hydrocarbons having boiling points from about 150°C to 216°C and light cycle oil hydrocarbons having boiling points from about 216°C to 370 °C.
18. A fluidized bed catalytic cracking system for the production of high yield of middle distillate products comprising hydrocarbons having carbon atoms in the range of C₈ to C₂₄ from heavy petroleum feeds, by a process as defined in claim 1, said system comprising at least two riser reactors (1 and 2) wherein, a fresh feed is introduced into the first riser reactor (1), typically, at the bottom section above regenerated catalyst entry zone through a feed nozzle (3), and at the end of the first riser reactor (1), the spent catalyst is quickly separated from hydrocarbon product vapors using separating devices (4) and subjected to multistage steam stripping to

remove any entrained hydrocarbons, and a conduit (5) feeds a part of the said stripped catalyst into a regenerating apparatus (7) and the other part of the stripped catalyst from the conduit (5) travels through another conduit (6) into a mixing vessel (10); and thereafter, the mixed catalyst from the mixing vessel (10) travels through a conduit (19) and is fed to the bottom of the first riser reactor (1), the hydrocarbon product vapors from the first riser reactor (1) which are separated from the catalyst in the separating devices (4) are fed to a vacuum or atmospheric distillation column (13) through conduit (12) whereby the first cracked hydrocarbon products are separated into a first fraction comprising hydrocarbons having boiling points less than or equal to 370°C and a second fraction comprising uncracked hydrocarbons with boiling points greater than or equal to 370°C ; the said second fraction comprising uncracked hydrocarbon products is fed through feed nozzle (16) into the bottom of second riser reactor (2) above the regenerated catalyst entry zone, and the regenerated catalyst from the regenerating apparatus (7) is fed to the bottom of the second riser reactor (2) through a conduit (9), and subsequently, the hydrocarbon products of the second riser reactor (2) are separated from the catalyst in separating devices (11), and the cracked products of the second riser reactor (2) along with the products of the first fraction of the first riser reactor (1) comprising hydrocarbons with boiling points less than or equal to 370°C are fed to a main fractionator column (15) which separates the said products into dry gas, LPG, gasoline, heavy naphtha, light cycle oil, heavy cycle oil, and slurry oil, and the entire heavy cycle oil and full or part of the slurry oil consisting mainly of hydrocarbons with boiling points greater than or equal to 370°C are recycled back to the second riser reactor (2) through a separate feed nozzle (17) located at a point lower than the position of introduction of main feed, and the feed and cracked product vapors travel along with the

catalyst, into the reactor wherein the spent catalyst separated from product vapors of the second riser reactor (2) in separating devices and the spent catalyst is subjected to multistage steam stripping for removal of entrained hydrocarbons and the stripped catalyst travels through a conduit (18) into the regenerating apparatus (7), wherein the coke on catalyst is burnt in the presence of air and/or oxygen containing gases at high temperature, and the flue gas from regeneration is separated from the entrained catalyst fines in separating devices (23) and the flue gas leaves from top of the regenerating apparatus (7) through a conduit (22) for heat recovery and venting through stack; the hot regenerated catalyst is withdrawn from the regenerating apparatus (7) and divided into two parts, one going to the mixing vessel (10) through the conduit (8) and the other directly to the bottom of the second riser reactor (2), and the mixed catalyst from the mixing vessel (10) is fed through the conduit (19) to the inlet of the first riser reactor (1), controlling the catalyst bed level in the individual or common stripper, the catalyst circulation rate from the common regenerator and the quantity of the spent and regenerated catalyst entering into the mixing vessel (10) using slide valves placed on the conduits and thereby producing high yield of middle distillate products.

19. A system as claimed in claim 1 wherein the separating device includes cyclone separator.
20. A process as claimed in claim 1 wherein pressure in the first and second riser reactors are in the range of 1.0 to 4.0 kg/cm²(g).

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 August 2001 (23.08.2001)

PCT

(10) International Publication Number
WO 01/60951 A1

(51) International Patent Classification: **C10G 51/04**

(21) International Application Number: **PCT/IN00/00013**

(22) International Filing Date: 16 February 2000 (16.02.2000)

(25) Filing Language: **English**

(26) Publication Language: **English**

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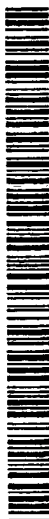
(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/60951 A1

(54) Title: A MULTI STAGE SELECTIVE CATALYTIC CRACKING PROCESS AND A SYSTEM FOR PRODUCING HIGH YIELD OF MIDDLE DISTILLATE PRODUCTS FROM HEAVY HYDROCARBON FEEDSTOCKS

(57) Abstract: According to this invention, there is provided a novel process and opposition for catalytic cracking of various petroleum based heavy feed stocks in the presence of solid zeolite catalyst and high pore size acidic components for selective bottom cracking and mixtures thereof, in a multiple riser type continuously circulating fluidized bed reactors operated at different severities to produce high yield of middle distillates, in the range of 50-65 wt% of fresh feed.

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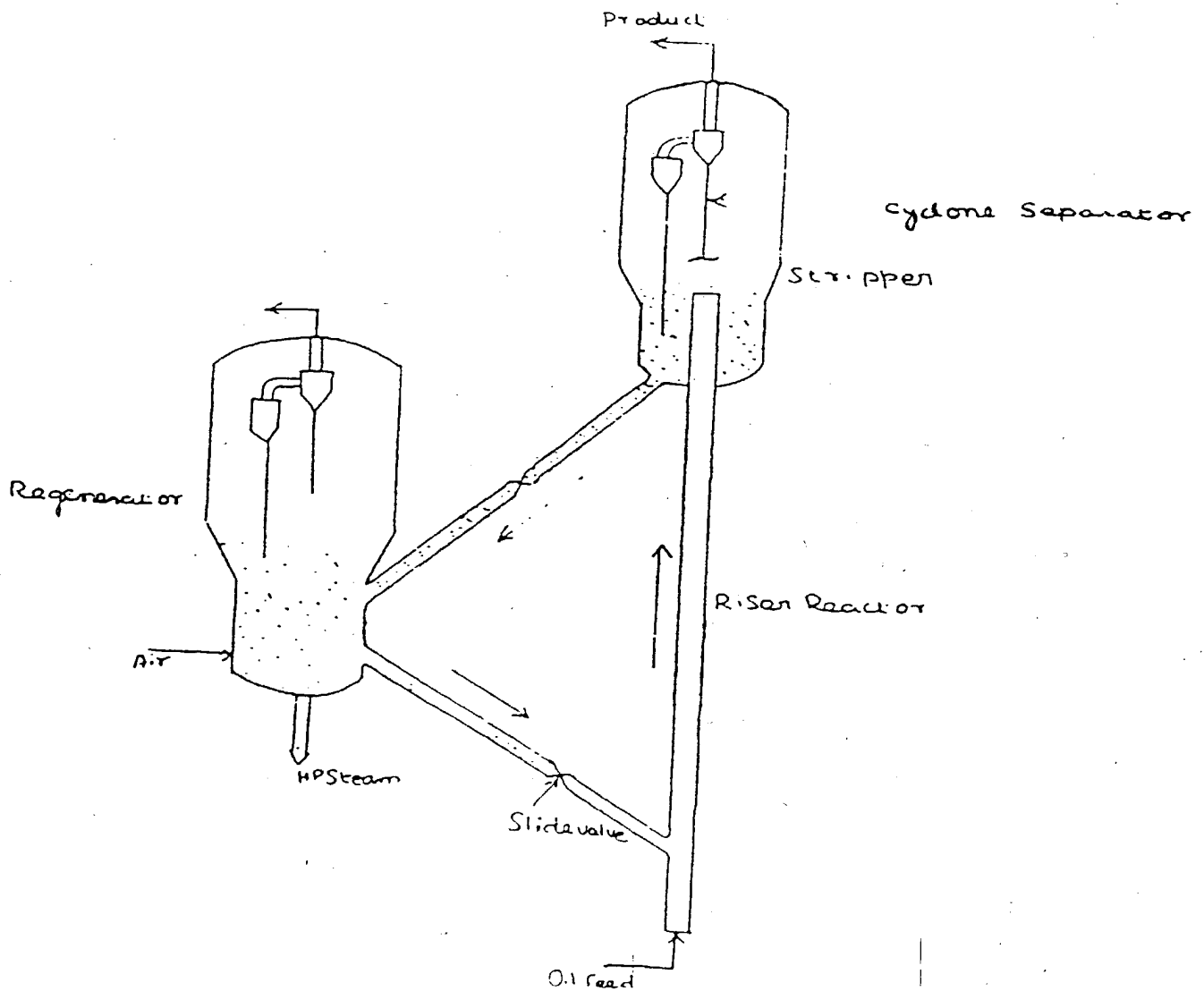


FIG.1

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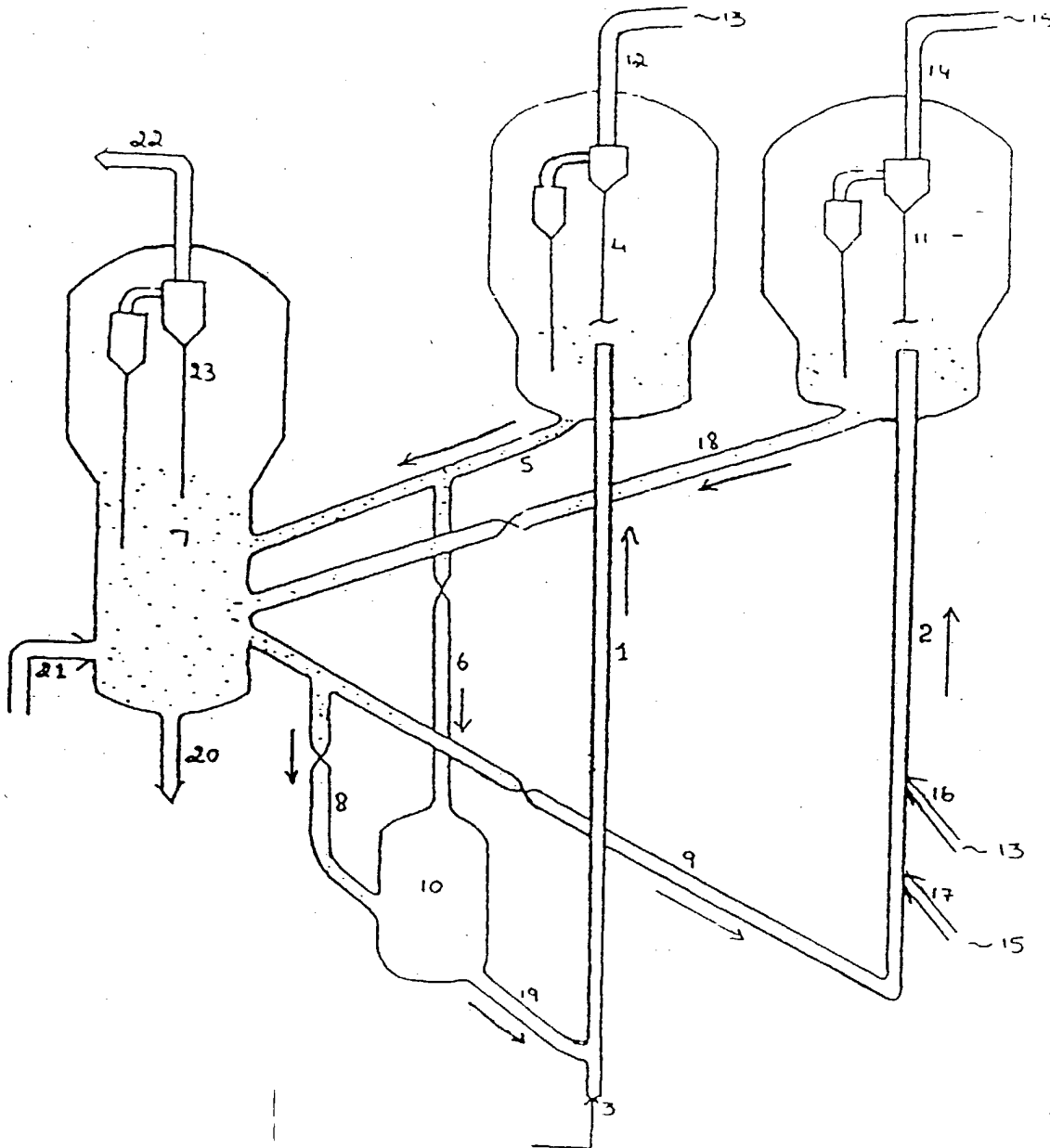


FIG.2

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[TCO / (Dry gas + LPG + Gasoline + Coke)] Vs.
- 370 deg. C Conversion

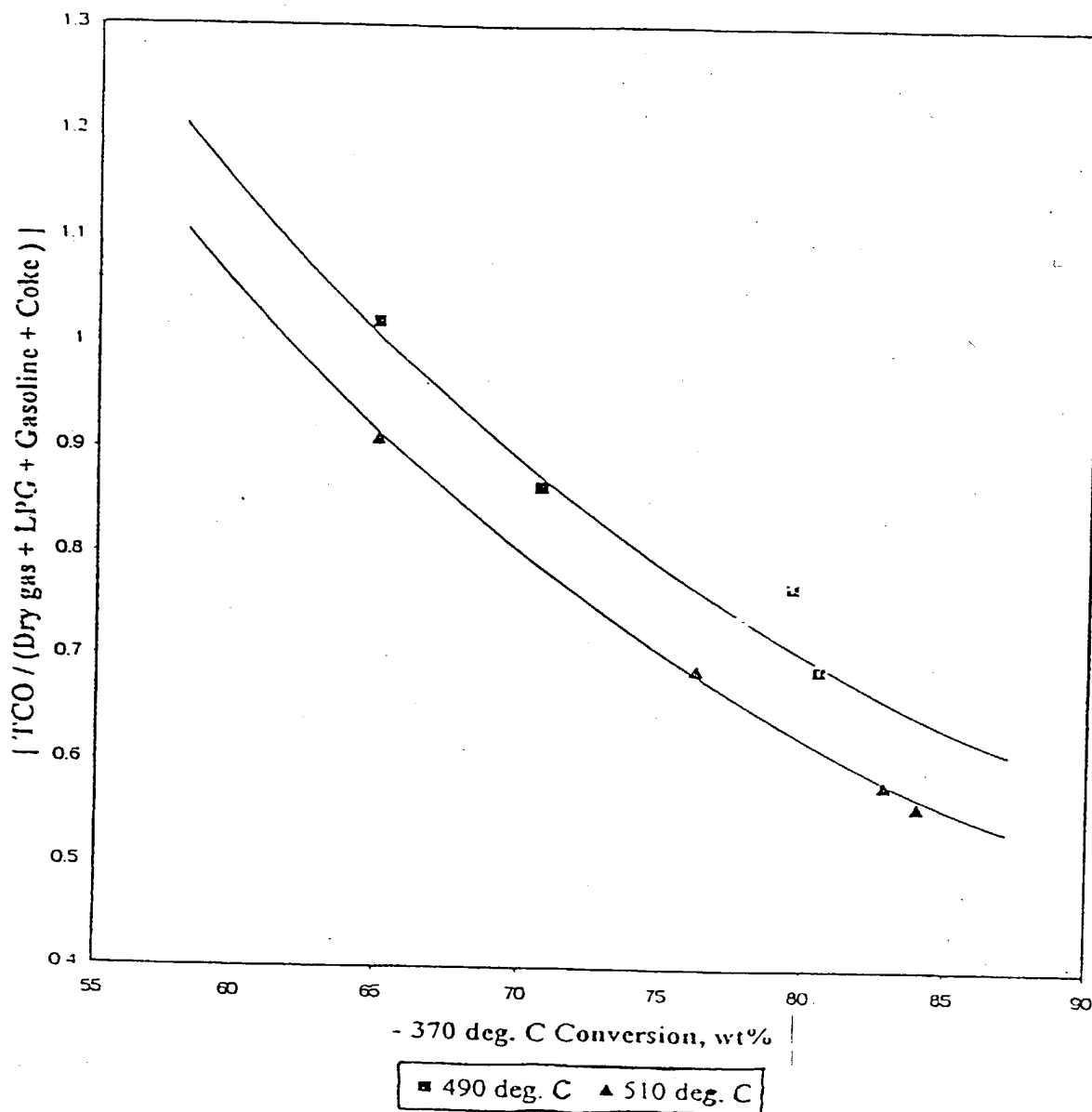


FIG.3

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Ratio of $\left[\text{TCO} / (\text{Dry gas} + \text{LPG} + \text{Gasoline} + \text{Coke}) \right]$ Vs.
- 370 deg. C Conversion

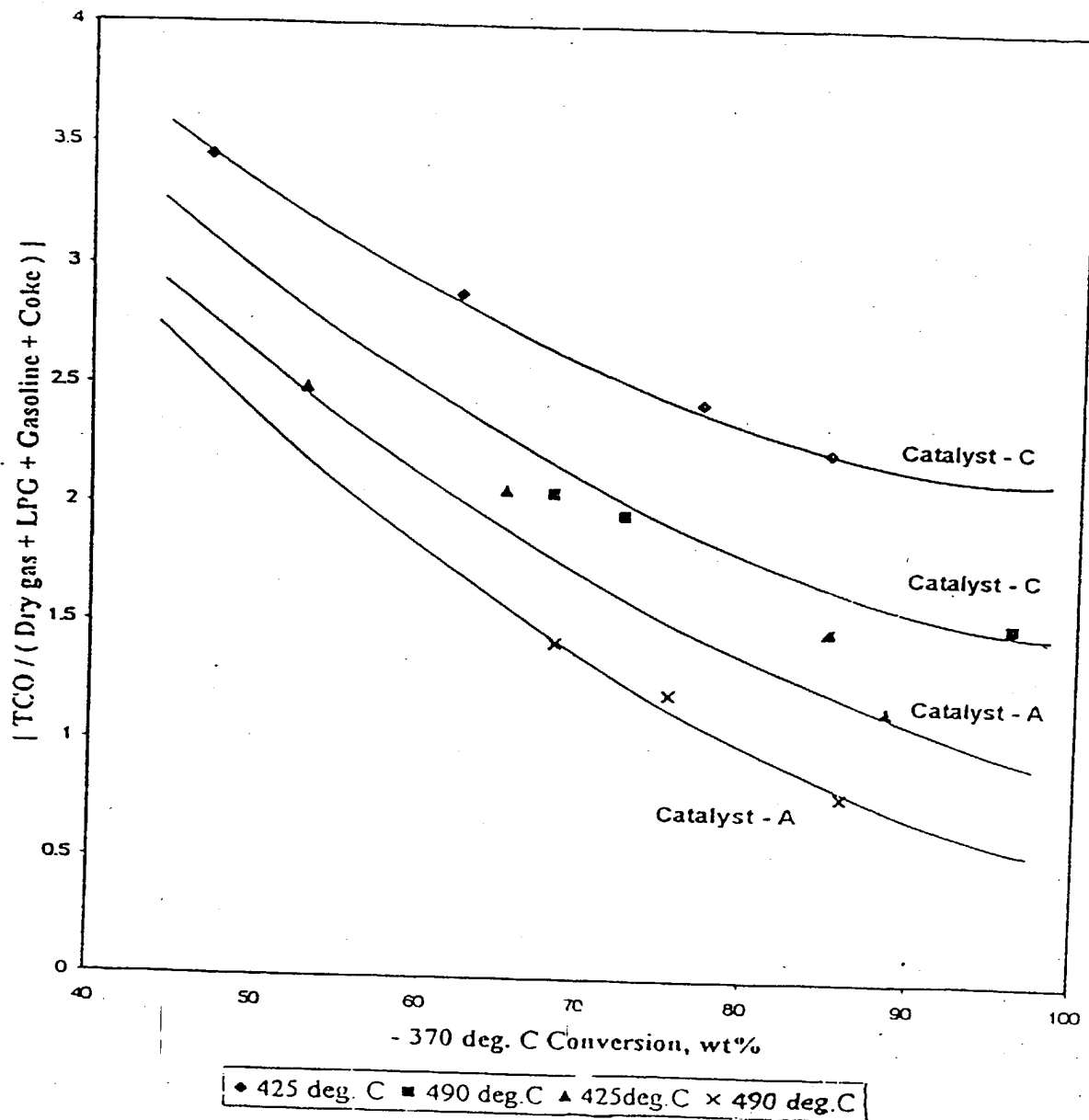


FIG.4

DECLARATION FOR PATENT APPLICATION AND APPOINTMENT OF ATTORNEY

As a below-named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe that I am the first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention (Design, if applicable) entitled: **A MULTI STAGE SELECTIVE CATALYTIC CRACKING PROCESS AND A SYSTEM FOR PRODUCING HIGH YIELD OF MIDDLE DISTILLATE PRODUCTS FROM HEAVY HYDROCARBON FEEDSTOCKS**

the specification of which (check one):

- ☐ is attached hereto.
☒ was filed on September 28, 2001 as Application Serial No. 09/937,850.
☒ was filed on February 16, 2000 as International Application (PCT) No. PCT/IN00/00013, and was amended on September 28, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with *Title 37, Code of Federal Regulations, § 1.56*. I hereby claim foreign priority benefits under *Title 35, United States Code § 119* of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which the priority is claimed.

PRIOR FOREIGN APPLICATION(S)

NUMBER	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
PCT/IN00/00013	INDIA	16.02.2000	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under *Title 35, United States Code, § 120* of any United States application(s) or PCT international application(s) designating The United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of *Title 35, United States Code, § 112*, I acknowledge the duty to disclose material information as defined in *Title 37, Code of Federal Regulations, § 1.56* which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

APPLICATION NUMBER	FILING DATE	STATUS (Patented, Pending or Abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine, or imprisonment, or both, under *Section 1001 of Title 18 of the United States Code*, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: I (We) hereby appoint as my (our) attorneys, with full powers of substitution and revocation, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Allan M. Lowe, Registration Number 19,641; Benjamin J. Hauptman, Registration Number 29,310; Michael G. Gilman, Registration Number 19,114; Kenneth M. Berner, Registration Number 37,093; and Randy A. Noranbrock, Registration Number 42,940.

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I hereby authorize the U.S. attorneys and agents named herein to accept and following instructions from **Kumaran & Sagar** as to any actions to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and the undersigned. In the event of a change in the person(s) from whom instructions may be taken, the U.S. attorneys will be so notified by the undersigned. ☒ See following page(s) for additional joint inventors.

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